

AMERICAN CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

LXIV.—ON A NEW METHOD OF DETERMINING GAS DENSITIES.¹

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In the well known method employed by Regnault for determining the density or specific gravity of air, oxygen, nitrogen, hydrogen, and carbonic acid, we deal primarily with tares, of which the weights to be determined are the differences. The glass balloon which holds the gas is tared by a similar balloon of exactly the same volume and of nearly equal weight, suspended from the opposite pan of the balance. The small difference of weight required to establish perfect equilibrium is alone measured with standard brass or platinum weights. Whatever may be the form of the subsequent calculation, the primary object is to obtain the tare of the empty balloon when absolutely vacuous. This known, the differences between such tare and the tare of the balloon filled with various aeriform substances, gives the weights of equal volumes of these substances under the temperatures and pressures at which the balloon was filled. The volume of the counterpoise is exactly adjusted to that of the balloon by the aid of a small subsidiary glass bulb (Plate II); and by sealing up more or less mercury in this bulb it is easy to make the difference of weight such that the standard weights required to complete the

¹ From the Proceedings of the American Academy of Arts and Sciences.

equilibrium will measure the differences of tare to be determined, and no more.

In the method of Regnault the tare of the empty balloon, or what was equivalent to it, was found by exhausting the balloon with an air-pump and weighing it after measuring the tension of the residual gas while the glass was surrounded by ice. But it has been shown by Agamennone¹ and Lord Rayleigh² that the results thus obtained are vitiated to a small extent by the circumstance that when the balloon is exhausted the pressure of the atmosphere determines a slight shrinkage of the external volume, which naturally disturbs the exactness of the compensation between the buoyancy of the air on the balloon and on its counterpoise. Although this shrinkage can be readily measured, as was done by Dr. T. W. Richards under my direction,³ and still more recently by Professor Crafts,⁴ who experimented on the balloon used by Regnault, which fortunately has been preserved, it seemed desirable to develop a method by which this correction could be avoided. For even if the new method should lead to no more accurate results than before obtained, it might serve to confirm the validity of the correction in question, and at least would give additional data towards establishing the value of important physical constants.

The new method we have devised for the purpose consists in first taring the balloon when filled with carbonic acid gas, and then drawing the gas through absorption tubes and determining its weight, as in the well known method of organic analysis. This weight known, the tare of the empty balloon is obviously the difference between the first tare and the weight in question. The practical problem here presented is, however, far more difficult than that of organic analysis. In the last we expect to determine the weight of only a few decigrams of carbonic acid within a few tenths of a milligram, while in the problem now before us we must weigh at least nine or ten grams of carbonic acid, not simply to a proportional, but to an equal, degree of accuracy. We only succeeded in securing such accuracy after many trials and a careful study of all the conditions involved, and our primary object in this

¹ Atti (Rendiconti) d. R. Accad. dei Lincei, 1885.

² Proceedings of the Royal Society 43, 362 (1888).

³ This Journal 10, 191 (1888); and Proceedings Am. Acad. 23, 177 (1888).

⁴ Comptes Rendus 106, 1662 (1888).

paper will be to describe the precautions which are essential to the success of the new experimental method. Incidentally it will appear that our results confirm in a most striking manner the high value of the specific gravity of hydrogen found by Lord Rayleigh,¹ and the low value of the atomic weight of oxygen found by ourselves.

The Balance and Weights.

The balance and weights were the same as those used by us in our previous work.² The disposition of the apparatus which, after many trials, we have found most suitable for accurate work, is shown in Plate II. The balance rests on the plank shelf of a wooden case, whose glazed doors are shown open in the drawing; and as this shelf is firmly secured to a thick brick partition wall behind, great steadiness is secured for the instrument. Around the inside of the wooden case are hung folds of drapery, which surround the balance case and protect the beam from radiations, while a curtain rolling on a spring fixture enables the experimenter to uncover the front as necessary. Fastened by flanges and screws to the under side of the same shelf is a box made of tinned sheet iron, of somewhat larger dimensions than the balance case. The front of this box can be almost wholly uncovered by means of two large doors made of the same metal sheet, and secured when closed by turning buttons, but shown open in the drawing. In the metal top are two circular holes about half an inch in diameter, corresponding to holes through the shelf and the base of the balance case, and directly under the centers of the balance pans. From hooks soldered to the under side of the pans the globe and its counterpoise are suspended by means of brass wires, and the lengths of the wires are so adjusted that the two glass vessels shall hang midway in the metal box. The globe is hung from a wire stirrup (Plate I), which swings from an eye at the end of one wire; while on the neck of the counterpoise is cemented a brass cap and hook, and both it and the small subsidiary bulb are hung on an eye at the end of the other wire. Of course these details might be varied. It is only important that the whole system should swing freely, with as little friction as possible, and that the balloon should be easily removed and replaced.

Through a third hole in the top of the metal box and shelf,

¹ Proceedings of the Royal Society **45**, 426 (1889).

² This Journal **10**, 92 (1888); and Proceedings Am. Acad. **23**, 159 (1888).

placed just in front of the balance case, passes a thermometer (not shown in the drawing) by which the temperature may be watched, and the inside of the box is painted with lamp-black so as to secure a uniform temperature throughout the interior. In our previous paper we spoke of the disturbance sometimes caused by currents of air within the box, but we found on further experience that these currents could be prevented by keeping the interior of the box as nearly as possible at the temperature of the external air. For this purpose it is important that the air of the room should circulate as freely as possible around the box, and the required condition is more easily secured if the box is made of thin metal sheet. It is also important that the temperature of the room should not be constantly changing, and that all circumstances should be avoided which would cause a flow of heat either into or out from the box. Sitting in front of the box in the process of weighing immediately causes a disturbance, and hence the division of the outer wooden case below the shelf is provided with wooden doors, which should be shut in front of the metal box before approaching the balance. When the thermometer hanging with its bulb inside the box indicates the same temperature as one hanging from the balance case outside within one-tenth of a centigrade degree, the conditions are most favorable for accurate weighing.

In order to maintain the atmosphere within the box in a constant hygrometric condition, we placed in it four large open dishes of sulphuric acid, two on the bottom of the box and two on a shelf near the top, as described in our previous paper. The acid was first boiled with a fraction of a gram of ammoniac sulphate, to remove the last traces of nitrous fumes, and renewed as occasion required.

We have found that we can most accurately estimate slight differences of weight with a balance thus loaded by observing the amplitude of the first swing of the pointer when the pans are relieved. With the balances of Becker, after the beam has been set on its bearings by the usual cam motion, the pans are still supported by two delicate arms, which are held by a weighted lever against the under side of the pans, but which can be pressed down by pushing against the button shown in the drawing on the front of the balance case. Such a mechanical arrangement is peculiarly adapted to this method of weighing, as it relieves the

pans suddenly and under the same conditions, so that the amplitude of the subsequent swing is an accurate measure of the difference of weight acting at the two ends of the balance beam; and in this case the inertia of the heavy load renders the effects surprisingly uniform. We give these details, not because they involve any new principles, but because the results have been reached after a long series of experiments, and our experience may save others much loss of time. With the apparatus arranged as we have described it, a difference of weight amounting only to one-tenth of a milligram was distinctly indicated, although the load exceeded half a kilogram on each pan, and the compensation was made so perfect that the equilibrium was not perceptibly altered by any ordinary changes of atmospheric conditions.

In order to reach such compensation, a counterpoise is first selected, which, on rough measurement, appears to be nearly of the same volume as the balloon, and at the same time a little lighter in weight. The apparatus is then mounted with this counterpoise as described, the stop-cocks of the balloon being closed. A series of observations are then made of the variations of weight arising from changes of atmospheric pressure and temperature, as carefully measured as possible. From such observations we can readily calculate, by the method we have previously described,¹ the volume of the small bulb required to make the compensation perfect, and an experienced glass-blower can readily make a bulb of the size indicated, which, before it is sealed, may be adjusted as to weight by loading with mercury as above described.

The weights used in connection with the balance had been adjusted for our previous work with the greatest care, and not only compared with each other, but also compared with a copy of the Washington standard. Although we shall deal in this paper solely with relative weights, yet the absolute values that may be deduced from our results must be correct far within the limits of the experimental errors of our own work. The sum of the weights required to measure the differences of tare never exceeded twelve grams, and of this small mass any possible difference between our copy and the Paris standard kilogram must be wholly inappreciable.

¹ Proceedings Am. Acad. 18, 55.

The Glass Balloon.

We have used in this investigation the same glass balloon that was fitted up for a somewhat different purpose in our work on the atomic weight of oxygen, but which has proved equally well adapted to determinations of gas density. Regnault in his work on the same subject used a balloon of ten liters' capacity, having its neck closed with a brass cap and stop-cock, and filled it by alternately exhausting the interior with an air-pump and refilling from a gasometer until the complete purity of the enclosed gas was assured. After long experience with this mode of experimenting, we have found it more convenient to fill the balloon by displacement directly from the generator, and we have found that we can reach a satisfactory result with least labor in this way.

Our balloon is represented in Plate I, which shows all the details of its construction. It was made by Emil Greiner of New York, and all the joints are so finely ground that when properly lubricated they will hold a vacuum indefinitely. The peculiar form of the stop-cocks enables the experimenter to shut into the globe a definite volume of gas and at the same time open a vent to the generator through the side tube; or to allow the gas to flow through the side tube until the current is perfectly pure before it is admitted to the balloon; and again, when the stop-cocks are both closed and the balloon disconnected, all the gas left in the connecting tubes will soon be replaced by air. At the freezing point the internal volume of the balloon, as nearly as we have been able to measure it, is 4961.5 cubic centimeters, and the weight of the glass 570.5 grams. After much experimenting, we have concluded that as great accuracy in determinations of gas density can be obtained with a balloon of this size as with a larger one. The advantage to be derived from the greater mass of gas experimented on is more than compensated by the greater liability to error which the weighing of larger vessels and the longer duration of all the processes involve.

The extent to which this balloon is actually compressed by the tension of the atmosphere when a vacuum is made in the interior has been carefully measured,¹ and amounts to 1.66 cubic centimeters for a difference of tension of 760 mm. between the interior and exterior of the glass vessel; and this corresponds to a loss of buoyancy of 1.96 milligrams in the air at 760 mm. and 22° C.

¹ This Journal 10, 193 (1888); and Proceedings Am. Acad. 23, 182 (1888).

When the balloon was not hanging on the balance, it was always protected by a metal case (see Plate II), from which the neck and connecting tubes alone protruded, and in transferring the balloon to and from the balance it was handled only by the neck.

In Regnault's experiments the balloon was filled with the gas under examination at the temperature of 0° C. by surrounding the glass with melting ice. This necessitates a careful cleaning of the globe at least twice during each determination, and thus may arise slight variations of condition to impair the accuracy of the results. We have found with Lord Rayleigh that it is preferable to fill the balloon at the temperature of the laboratory, but we must then observe the temperature with very great accuracy. It is important to know the temperature to the one hundredth of a centigrade degree, for even so small a difference of temperature as this causes a change in the amount of carbonic acid gas which our balloon will hold under ordinary atmospheric conditions corresponding to three tenths of a milligram.

We have found it possible to secure even such constancy of temperature as this delicate measure implies by placing the balloon while filling in a calorimeter case, and observing the temperature with a calorimetric thermometer divided to the fiftieth of a centigrade degree. The calorimeter case consists of a cylindrical vessel of sheet zinc wide enough to receive the balloon with its tube and leave a play of less than an inch on either side. This vessel is fastened by metal stays inside a second cylindrical vessel of the same material, leaving an annular space about two inches wide and an equal space between the bottoms of the two vessels, all of which is filled with water. In addition, the outer vessel is further protected by a layer of felt one inch thick, kept in place by an outer covering of the same sheet metal. When in use, the top is covered by a cap made also of thick felting, and in the crown of the cap is a slit, through which a thermometer may be inserted or the hand passed to turn the stop-cocks. The gas to be used is conducted into the calorimeter through a very small lead tube, which is connected with the lower tubulature of the stop-cock by a rubber connection, and the balloon is so placed that the current shall enter either at the top or at the bottom of the vessel, according as the gas is lighter or heavier than the atmosphere. The calorimeter case stands about four feet high, and the balloon rests in it on a down cushion, with the connecting tubes fully six inches

below the surface of the water in the annular space above mentioned. With this apparatus it was possible to keep the temperature of the balloon constant within the one hundredth of a centigrade degree for an hour at a time, unless the temperature of the laboratory suddenly and greatly changed.

The general arrangement for filling the balloon was then as follows. The gas delivered from the drying tubes of one of the generators hereafter to be described passed through the lead tube of which we have spoken to one or the other, as the case might be, of the tubulatures of the balloon standing in the calorimeter. Passing out by the opposite tubulature, the current was conducted by a similar lead tube to a second but much larger balloon serving as a gasometer, and from the last vessel through a gas wash-bottle to the atmosphere. The bottom of the wash-bottle was covered with strong sulphuric acid to dry any returning air, but not deep enough for the inlet tube to dip under the liquid. The current was continued until the proper test showed that the gas issuing from the end of the apparatus was perfectly pure. Then the inlet cock of the balloon was turned, and the temperature of the calorimeter case watched until constant, and a sufficient time had elapsed to establish a perfect equilibrium with the atmosphere through the connecting tubes and vessels. This, as we found by experience, often requires longer time than we were led to anticipate, and when experimenting with carbonic acid gas it is not safe to allow less than twenty or thirty minutes; and now the large balloon and wash-bottle come into play to prevent air diffusing into the balloon, or being drawn back in consequence of changing pressure.

When all the conditions seemed to be satisfactory, the temperature of the calorimeter and the height of the barometer were accurately observed, the first to the hundredth of a centigrade degree and the last to the twentieth of a millimeter, noting always the height of the attached thermometer. The hand was then quickly thrust into the calorimeter, and the outlet cock at once closed. The balloon was now removed, dusted with a large camel's-hair brush, and hung in its place on the balance. When, however, the atmosphere is very dry, as it often is in this climate during the winter months, it may happen that the surface of the glass acquires a charge of electricity from the friction of the cushion in the calorimeter or of the brush just mentioned; and if there is any suspicion of such an effect, the best way to dissipate the

charge is to stand the balloon for a few minutes in its metal case (shown in Plate III), after covering the bottom of the case with a thin layer of water. If the balloon is hung on the balance with a charge of electricity on its surface, however small, it will be unequally attracted by the surrounding metallic walls, and most confusing anomalies of weight will be noticed. Moreover, in the very dry atmosphere of the case the charge will last for days, or even weeks, as on the insulated vanes of an electrometer.

Thermometers and Barometers, and their Correction.

The thermometers on whose indications we have relied in this investigation are two of small range, but divided into fiftieths of a centigrade degree and made by the house of the late Dr. H. Geissler of Bonn. We were obliged to use the two, for our investigation was continued into summer weather, which exceeded the range of the thermometer first selected. As should always be the case with such instruments, the zero point is given in each case on a short subsidiary scale, separated from the main scale by an enlargement of the tube. Careful observation showed that the zero point of the instrument we will designate as No. 1 was depressed 0.02 of a centigrade degree, while the zero point of No. 2 was raised 0.28 of a degree. Making the correction thus indicated, to be added to all temperatures observed with No. 1, and subtracted from all observed with No. 2, the two instruments were found to agree exactly through all portions of the scale common to both. Obviously, therefore, the differences of temperature observed are perfectly trustworthy to the one hundredth of a degree, but how far the absolute values—counting from the freezing point of water—can be relied on when compared with the observations of other experimenters, we have no means of determining. Of course, it will be understood that all temperatures hereafter given have been corrected for the variation of the zero point. At the close of the investigation the zero points were again tested and found to be unchanged.

The barometer used was a large standard instrument of the familiar mountain form, made by Greene of New York. Hanging at the side of it was a smaller instrument of the same maker, whose indications agreed with the first within the tenth of a millimeter. Here again, as in the case of the thermometer, there can be no question as to the accuracy of the differences of tension observed

within moderate limits; but how far the absolute heights can be compared with those observed by Regnault and others is also a problem that cannot be readily solved, and one not within the means of a single experimenter to determine. All heights of barometer given hereafter have been reduced to 0° by the tables of Guyot.¹

Tare of the Empty Balloon by Regnault's Method.

In the method of experimenting devised by Regnault the tare of the empty glass globe used, although not explicitly given, was implicitly determined. His arrangement for filling the globe, shown by Figure 1, has already been referred to, and his general method of experimenting consisted in taking the tare of the globe when filled with the same gas at the temperature of melting ice under as different tensions as possible. The tensions were found by measuring with a cathetometer the difference of height, $\alpha\beta$ (see Fig. 1), under each condition, and the tares were found by means of the balance by the system of compensation already described. The difference of tare gives the weight of gas which the globe contains at 0° at the tension $H-h$, and from this may readily be deduced the weight at any other tension; as, for example, at the standard tension of 760 mm. The calculated weight at either of the tensions H or h , deducted from the corresponding tare, gives what we have called the tare of the empty globe; but obviously with Regnault's method this value is not needed in the calculations of specific gravity or density.

When the globe is filled by displacement it conduces to greater accuracy to determine independently the tare in question; and as soon as the details of the new method had been worked out, we began our final determinations by taking, according to the old method, the tare of the balloon above described when empty, so as to obtain a definite standard of comparison for further results.

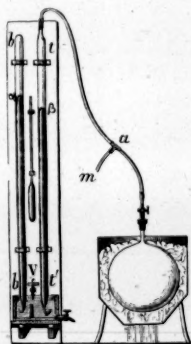


FIG. 1.

¹ Published by the Smithsonian Institution, Washington.

We, however, varied the method of Regnault in so far that we always filled the globe with hydrogen before exhausting the interior. As with this exceedingly light material the weight of the residual gas seldom exceeded one half a milligram, an error as great as one fifth in the capacity of the balloon or in the tension of the residual gas would cause no appreciable difference in the value of the small weight we sought to estimate. The details of a single example will be sufficient to illustrate the procedure.

Determination No. 1.

A current of hydrogen gas from the electrolytic generator described in our previous paper¹ was run through the balloon from Saturday, May 25th, at 4 o'clock P. M., to Monday, May 29th, at 10 o'clock A. M., 1889, the balloon standing in calorimeter case connected with larger balloon to receive overflow. At moment of closing, the height of barometer and temperature of the case were observed, but these data are not required for the present determination, and will be given hereafter when used for calculating the specific gravity of hydrogen. The balloon was exhausted with an excellent mechanical air-pump,² and the tension of the residual gas measured by means of a siphon manometer interposed between the balloon and the pump. The form of manometer used is shown by Figure 2. It was made in the laboratory, and in filling it with mercury the liquid metal, purified by repeated distillation, was boiled in the tube with the greatest care. For convenience, the difference of level of the mercury in the two arms was measured with a cathetometer constructed by the Société Genevoise, but it might have been estimated with sufficient accuracy by the millimeter scale of the instrument. Tension in balloon after exhaustion $456.95 - 455.55 = 1.40$ mm.

Assuming 0.4164 as the approximate value of the weight of hydrogen gas filling the balloon at 763.10 mm. and $21^{\circ}.08$ C. (p. 535), the weight of the residual gas at 1.4 mm. and same temperature would be 0.00076 gram or 0.76 mg. No exact observation of the temperature of the balloon was necessary; for a difference of 4° C. would not alter the above value more than $\frac{1}{100}$ mg. and we may therefore assume that the temperature of the balloon

¹ This Journal 10, 702 (1888); and Proceedings Am. Acad, 23, 168 (1888).

² Author's Chemical Physics, p. 331.

was the same as that of the laboratory, which at the time was 21° C. The correction for lessened buoyancy (increased weight) on account of the contraction of the balloon by atmospheric pressure amounts, as has been shown, to 1.98 mg.,¹ and this added to 0.76

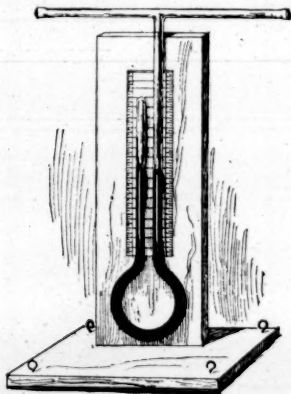


FIG. 2.

makes the total correction 2.74 mg. When the balloon was hung on the balance, the weight required to complete the tare was 2.5600 grams. Hence we have:

Weight of balloon exhausted, ...	2.5600	grams.
Correction for residual gas, ...	0.76	mg.
" " lessened buoyancy, 1.98 "	27	"

Tare of empty balloon, ... 2.5573 "

Two other determinations were made in the same way, and the three results are united in the following table.

Summary.

Tare of empty balloon, 1st value, ...	2.5573	grams.
" " " 2d "	2.5572	"
" " " 3d "	2.5574	"
Mean value, ...	2.5573	"

¹ This Journal 10, 194 (1888); and Proceedings Am. Acad. 23, 184 (1888).

Tare of the Empty Balloon by Chemical Method.

The general theory of this method has already been stated. The balloon is filled with carbonic acid gas by displacement, and the tare taken. The gas is then drawn through a series of absorption tubes, as in the process of organic analysis, and the sum of the increased weights of these tubes gives the weight of the total contents of the balloon at the time the tare was taken. The weight of the balloon filled with carbonic acid gas less the weight of the carbonic acid thus determined is obviously the tare of the empty balloon required. In attempting to perfect this apparently simple experimental method we met with unexpected difficulties, arising from several circumstances.

In the first place, in order to wash out from the balloon the last traces of carbonic acid, it was necessary to draw through the apparatus a very large volume of air, and the system of purifiers and desiccators needed absolutely to free the atmospheric air from the least admixture of carbonic acid or aqueous vapor was found to be far more extensive than we anticipated. In the second place, since the globe held, at the ordinary temperature of the laboratory and at the average pressure of the atmosphere, no less than nine grams of gas, the common potash bulbs used in organic analysis were wholly inadequate for our requirements, and we only succeeded after many trials in finding a form of apparatus by which so great an amount of carbonic acid could be determined with the necessary accuracy, that is, within a few tenths of a milligram. The arrangement finally adopted is shown in Plate III. The balloon is represented standing in its covered metallic case, in which it is placed the moment it is taken from the balance. On the right of the balloon and below it is a system of tubes for purifying and drying the atmospheric air which enters from outside the laboratory by the flexible tube on the extreme right. On the left of the globe is a system of tubes for absorbing the carbonic acid. The flexible tube on the left is connected with a Bunsen pump through a form of Mariotte's flask,¹ and by this means a current is maintained through the whole system, under constant pressure.

Purifying and Drying Apparatus.

The air entering as we have described, passed first through a wash-bottle of familiar construction, containing a solution of potassic

¹ This Journal 10, 96 (1888); and Proceedings Am. Acad, 23, 163 (1898).

hydrate, sp. gr. = 1.44, and then through a similar wash-bottle containing a concentrated solution of baric hydrate; and if the rapidity of the current was not greater than two bubbles a second, this double washing was found sufficient to remove the last traces of carbonic acid. Indeed, as soon as the baryta water showed the least indications of cloudiness, the solutions were renewed. It was not so easy to remove the last traces of moisture.

After the air had passed the washing flasks it entered a system of desiccators, shown in the lower half of the plate, where in small bubbles it travelled up first one tube, and then a second tube, both 5½ feet long, and filled with concentrated sulphuric acid previously boiled with a small amount of ammoniac sulphate to remove all nitrous fumes. Leaving the second of these tubes it entered an elongated bulb four inches long by two inches in diameter filled with phosphoric anhydride; and the fact that prolonged contact with sulphuric acid is not sufficient to remove the last traces of moisture, was shown by the circumstance that after the current has passed for several days the dry white powder at the opening of the bulb showed signs of deliquescence.

Our phosphoric anhydride was prepared by burning common yellow phosphorus in a large sheet-iron drum, through which a current of dry air was drawn with sufficient rapidity to maintain the phosphorus in rapid combustion, and the bottom of the drum was made tunnel-shaped so that the anhydride could be shaken down into a self-sealing fruit jar as fast as it formed. As thus prepared the anhydride has a slight odor, which it loses after a prolonged current of dry air has been drawn through the powder; and after our drying tubes had been filled, their contents were submitted to a preliminary treatment of this sort, and not until long after all perceptible odor had disappeared were they used in our work. We noticed that after the anhydride had been used for some time it appeared more granular and lost in part its hygroscopic power. In order to make sure of this point, the apparatus as far as described having been in use for several weeks, we connected with the first phosphoric anhydride tube a weighed tube containing fresh anhydride. After drawing air through the system at the same rate and during the same time as in a carbonic acid determination, we reweighed this second tube and found that it had gained 5.5 mg. We next added to our system the U tube filled with phosphoric anhydride, which is shown in Plate III immedi-

ately before the balloon, and repeated the experiment. There was then no gain in weight perceptible. The observations were as follows:

Before interposing the U Tube.

		H.	T°.	R.
1st weight P_2O_5 tube,	25.9212 grams.	295.7	20.0	302.7
2d " "	25.9267 "	295.2	20.8	301.4
	0.0055 "			1.4

After interposing the U Tube.

1st weight P_2O_5 tube,	25.9268 grams.	299.3	19.6	306.7
2d " "	25.9268 "	299.2	21.6	304.6
				2.1

In this table the column headed H contains the barometric pressure at time of weighing in tenths of an inch; that headed T° gives the corresponding temperatures of the balance case in centigrade degrees. By adding to the values H the quantities $(27 - T)^\circ$ we obtain the values R, and these are the barometric heights which would give an atmosphere of the same density, and therefore exerting the same buoyancy, as the atmosphere at the time of weighing if the temperature were uniformly $27^\circ C$. The correction that should be made for differences of temperature and pressure at successive weighings can at once be calculated from these values. We found by experiment that for the phosphoric anhydride tube used in these and in subsequent determinations, the correction amounted to 0.04 mg. for each tenth of an inch change of pressure, and hence in the above weighings the correction is too small to be appreciable. This simple method of correcting weights for changes in the buoyancy of the atmosphere has been described in a previous paper.¹ In order to apply it readily, the barometric heights, although usually read in millimeters, were often also noted, as here, in tenths of inches, and the instrument we used was provided with both scales.

It is obvious from the above experiments that the hygroscopic power of phosphoric anhydride becomes impaired before the powder actually deliquesces, and we have dwelt on the point because the experience was of great importance in our investigation by

¹ Proceedings Am. Acad. 18, 55.

leading us to add the second anhydride tube to our system, and also to watch carefully the condition of its contents, and to replace the tube as soon as the least change was perceptible. We attribute the change to a glazing of the amorphous grains due to the forming of a coating of glacial phosphoric acid, but the effect is one that would not be noticed except under such extreme conditions as existed in our work. We now pass to the system of absorption tubes on the other side of the balloon.

Absorption Apparatus.

The apparatus for the absorption of the carbonic acid gas must meet very opposite requisitions. In the first place, it must offer a sufficiently large mass of absorbent to the pure gas which first comes to prevent overheating from the rapid chemical combination. In the next place, it must be capable of removing the last traces of carbonic acid from the air which is afterwards drawn through the tubes. Lastly, it must not be so heavy or so complicated that it cannot be promptly and sharply weighed, and the correction for changes of temperature and pressure between successive weighings accurately estimated.

After trying in various ways to enlarge and modify the different forms of potash bulbs and spiral tubes in general use (and in these attempts we had the aid of a skilful glassblower), we found that we could reach a more accurate result with a system of separate tubes, in spite of the number of weighings they involved. To absorb the great mass of the carbonic acid we used the simplest form of gas-washer, shown in Plate III, at *A*. The bulb had a capacity of 200 cc., and in this we placed 75 cc. of a solution of potassic hydrate having sp. gr. = 1.443. When empty the bulb weighed only 57 grams, and when filled about 165 grams. Assuming that the potash was fully neutralised, less than one half of this amount would be sufficient to combine with nine grams of carbonic acid; but to insure prompt action and avoid excessive heating the amount given is required.

The potash tube was followed by a small U tube, four inches long, with ground caps filled with finely granulated soda lime, and weighing when full about 40 grams. (See *B*, Plate III.) To this was united a similar U tube containing phosphoric anhydride to hold the aqueous vapor, which is brought over by the gas current in no inconsiderable amount from the potash solution and the

soda lime, in consequence of the heat set free by the absorption. The anhydride tube weighed when full about 25 grams, and is shown at *C*. Next was a third U tube filled with glass beads and having a few drops of strong sulphuric acid at the bend. This tube, *D*, was not weighed, but was necessary in order to indicate any sucking back of the air and to prevent any vapor from thus reaching the phosphoric anhydride. The double bulb forming the end of the system, shown at *E*, was made by melting together the usual inlet tubes of two gas-washers like *A*. In this we placed 50 cc. of a standard solution of baric hydrate, and the peculiar construction was necessary in order to provide against regurgitation in consequence of back pressure. The solution is easily washed out of the bulbs, and when retitrated at the end of the process gives the amount of carbonic acid, if any, which escaped the other absorbents. All of these tubes were united into one system by rubber connections carefully lubricated both inside and out with vaseline, a soft paraffine which had previously been melted and heated to remove every trace of moisture.

The manipulation of this apparatus was an interesting experiment. When all had been set up as shown in Plate III, the globe being full of carbonic acid, the Bunsen pump was first started, and after a constant suction (regulated by the Mariotte's flask before described) had been established, we cautiously opened the cock of the balloon, which connected with the potash bulb, closely watching the flow of gas. As soon as this flow began to slacken, we as cautiously opened the farther cock, by which air was admitted to the balloon through the line of purifiers, still closely watching and regulating the flow. We then noticed a striking phenomenon. As pure carbonic acid was now passing into the potash bulb, the air mixing but slowly with the heavy gas at the surface of contact as the level sunk in the balloon, the absorption at first was complete. If the air supply from behind was not sufficient, a partial vacuum formed in *A*, and air was drawn back through the tubes in front, as indicated at once by the bubbles at the bend of *D*; but if the supply was carefully regulated, a perfect equilibrium could be maintained in the tubes beyond, and we have seen the carbonic acid flow into the potash bulb for half an hour without more than a few bubbles of air passing through the sulphuric acid at the bend of *D* in either direction.

After a while, however, when the great mass of the carbonic acid

has been absorbed, bubbles of air begin to pass through *D*, and also bubble through the baryta water beyond, and soon a steady current is established throughout the whole apparatus, which may then be left to take care of itself. If the current does not exceed in rapidity two bubbles a second, it may be allowed to flow for twenty-four hours without risk, and in that time every trace of carbonic acid will have been washed out of the balloon. The suction should now be stopped, and the cocks of the balloon closed. The tubes *A*, *B*, and *C* may then be disconnected, and after they have come to equilibrium in the balance case reweighed. The double bulb *E* must also be disconnected, the baryta washed out into a suitable bottle, and the solution retitrated with oxalic acid.

As the weights of the tubes *A*, *B*, and *C* must be corrected for the buoyancy of the air, it is essential to note the temperature of the balance case and the height of the barometer at the time of each weighing. The corrections in question may be considered under two heads; first, that made necessary by a change of temperature or pressure between successive weighings; secondly, that required to eliminate the effect of atmospheric buoyancy on the total weight of carbonic acid absorbed.

The first correction is best made by the method already described, and the application of this method was greatly facilitated in the present investigation by the circumstance that the same tubes, with the same weights of contents, were used in all the carbonic acid determinations made. We were able to determine once for all for each tube the correction required for a variation of one tenth of an inch in the barometric height reduced to 27°C .,¹ and the correction in any case could be found by a simple multiplication. Thus we estimated that the correction for one tenth of an inch in the barometric height reduced to 27°C . was:

For the potash bulb before absorption,	. .	0.306 milligram.
" " " after	. .	0.321 "
" soda lime tube,		0.067 "
" phosphoric anhydride tube,		0.040 "

¹ That is, reduced to the height which would be required to give at the temperature of 27° , an atmosphere of the same density and buoyancy as that at the temperature of the balance case when the tube was weighed. See *Proceedings Amer. Acad.* 19, 55.

Calculation of Correction for Potash Bulb.

	Before Absorption.	After Absorption.
Weight of glass, ...	57.45 grams.	57.45 grams.
Volume of glass = $57.45 \div 2.5$, ...	23 cc.	23 cc.
" KOH solution, ...	75 "	80 "
	98	103
" brass weights, $164 \div 8.2$, 20 "		
" " " $173 \div 8.2$, ...		21 "
Uncompensated volume, ...	78 "	82 "
Air displaced at 27° C. and 300 tenths of an inch.		
1.176×78	91.928 mg.	
1.176×82		96.332 mg.
Variation for $\frac{1}{300}$, ...	0.306 "	0.321 "

The correction of the total weight of carbonic acid for the buoyancy of the atmosphere was not so simple a problem; but by using the same bulb and nearly the same volume of the same solution of potassic hydrate in every case, it was sensibly the same for all the determinations. The specific gravity of the solution of potassic hydrate before the absorption was 1.443, and tested in two separate determinations after absorption it was found to be 1.464 in each case. Using now the arithmetical means of the weights of the potash bulb in the three determinations under consideration, it was easy to find an average value for the correction thus:

Average weight of potash bulb before absorption,	165.02 grams.
Weight of glass, ...	57.45 "
" solution of KOH, ...	107.57 "
Volume of solution of KOH = $107.57 \div 1.443$, ...	74.55 cc.
Average weight of potash bulb after absorption, ...	173.57 grams.
Weight of glass, ...	57.45 "
	116.12 "

Volume of solution of KOH = $116.12 \div 1.464$, .	79.32 cc.
Difference of volume = $79.32 - 74.55$, ...	4.77 "
Weight of CO ₂ absorbed in potash bulb = 173.57 — 165.02 , ...	8.55 grams.
Volume of brass weights = $8.55 \div 8.2$, ...	1.04 cc.
Uncompensated volume = $4.77 - 1.04$, ...	3.73 "
Weights of 3.73 cc. of air at 300 tenths inch and 27° C. = 1.176×3.73 = corr. required, .	4.39 mg.

In this calculation we have necessarily left out of the account both the small amount of carbonic acid absorbed by the soda lime and the water carried by the current from the potash bulb to the connecting tubes; for the increased weight of these tubes results from both these causes, whose relative effects or whose influence on the correction we cannot estimate. That they would tend to raise slightly the value of the correction is obvious; and if we assume, as we have in the following calculations, that the value is 4.5 milligrams, we shall approximate as nearly to the precise amount as circumstances will permit. For all these corrections the data are only known within certain narrow limits; but the total uncertainty thus arising does not exceed two or three tenths of a milligram in the final result.

In weighing the potash bulb and U tubes it is of course essential that they should be left in the balance case until a perfect equilibrium of temperature has been reached, and then they must be weighed when open so that a perfect equilibrium of pressure on the inside and outside of the glass may be secured. And since we were here aiming at very great accuracy, we felt it important to inquire further whether any gain of weight from hygroscopic moisture was possible during the time necessary to verify the weight while the tubes remained open on the scale pan. We therefore carefully investigated this point. The air in the balance case was kept as dry as possible by an open dish of sulphuric acid, and the experiments were made under such conditions. It was found that the weight both of the potash bulb and of the soda lime tube remained absolutely constant, hour and hour together, except so far as they were influenced by changes of temperature and pressure, but the weight of the phosphoric anhydride tube slowly but uniformly increased at the rate of 0.025 mg. per hour. We followed the change on one occasion from 10 h. 45 m. A. M. to 6 h. 15 m. P. M., and during these seven hours and a half the gain was 1.9 mg., while the changes of temperature and pressure

meanwhile were not enough to cause a sensible difference in the atmospheric buoyancy. Such experiments were continued for a sufficient length of time to enable us to confirm the values of the corrections above given, and they gave us great confidence in our

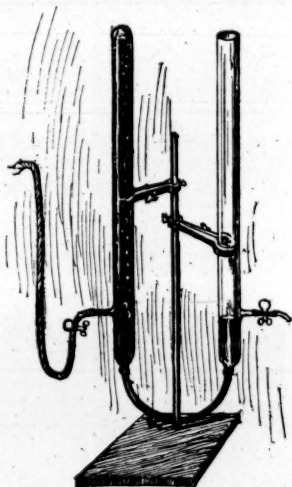


FIG. 3.

weights. They showed that the only precaution necessary for accuracy was to close the tubes as soon as they were disconnected, and to leave each of them closed in the balance case until it was time to take the weight. The U-shaped tubes with perforated ground stoppers, by which connection with the lateral tubes can be instantly opened or closed, are admirably adapted to this work. As an example, we give next the details of one determination of carbonic acid by the method we have described

Details of a Determination of Carbonic Acid.

The gas was generated from statuary marble and dilute hydrochloric acid in an apparatus precisely similar to that described and figured by us in a previous paper.¹ It was first washed

¹ This Journal 10, 100 (1888); and Proceedings Am. Acad. 23, 166 (1888).

by a solution of potassic bicarbonate, and then, having passed in succession over calcic chloride, sulphuric acid, and phosphoric anhydride, it was conducted into the balloon and overflow in the manner already described. The gas was tested by leading the current from the overflow into a familiar form of nitrogen apparatus filled with a solution of potassic hydrate (Fig. 3), and not until no measurable residue was left by a full liter of gas was its condition regarded as satisfactory. The balloon stood in the calorimeter case, and when the cocks were closed with the precautions already described, the temperature of the case and the height of the barometer were observed, and although these values are not needed for determining the tare of the empty balloon, they will be used for determining the density of carbonic acid hereafter. The balloon was then disconnected and hung on the balance, and its tare found to be

$$W = 11.5907 \text{ grams.}$$

The balloon was then transferred to its metal case, and, having been mounted as shown in Plate III, the determination of the weight of its contents proceeded as just described.

Potash Bulb.

	Grams.	H.	T°.
1st weight of potash bulb,	165.3388	299.99	25.8
2d " " "	174.0132	299.83	27.0
	8.6744		
Correction ¹ for change of H and T,	4		
	8.6740		

¹ Since the volume and density of the potash solution used were closely the same in all the determinations, whether compared before or after the absorption, the value of the correction may be assumed to be the same in all cases, and, as has been shown at page 526, amounts to 0.306 mg. before absorption and 0.321 mg. after absorption for every change of one tenth of an inch pressure or 1° centigrade temperature from the standard of 300 tenths inch and 27° C. or 300° absolute temperature. The correct mode of calculating the correction in any case is to reduce both weights to what they would appear to be at H = 300 and T₀° = 300 = 27° C. before taking their difference, using the value 0.306 for the smaller of the two, and 0.321 for the larger.

299.89 at 25.6° corresponds in buoyancy to 301.09 at 27°.
 299.83 at 27° " " " " 299.83 " "
 301.09 - 300 = 1.09 and 1.09 × 0.306 = 0.33 additive.
 299.83 - 300 = -0.17 and -0.17 × 0.321 = -0.05 subtractive.
 Then 165.3388 + 0.33 = 165.33913
 174.0132 - 0.05 = 174.01315
 8.67402 as before.

As regards the sign of the correction, notice that, when reduced to H = 300, the buoyancy becomes less and the *apparent* weight greater if the previous pressure was above 300, and *vice versa*.

Soda Lime Tube.

	Grams.	H.	T°.
1st weight of soda lime tube,	42.8731	299.54	26.6
2d " " " "	43.1857	299.87	27.4
Correction insensible,	0.3126		

Phosphoric Anhydride Tube.

1st weight of anhydride tube,	39.5196	299.50	27.0
2d " " " "	39.5493	300.00	27.2
Correction insensible,	0.0297		

Standard Solution of Baric Hydrate.

Before absorption, 50 cc. required 46.60 cc. solution of oxalic acid.							
After " " " "	43.65	"	"	"	"	"	"
	2.95						

One cc. of decinormal solution of oxalic acid contains 0.0126 gram of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, corresponding to 0.0044 gram of CO_2 .

$$2.95 \times 0.0044 = 0.0130 \text{ gram of } \text{CO}_2.$$

Total Weight of Carbonic Acid.

	Grams.
From potash bulb, ...	8.6740
" soda lime tube, ...	0.3126
" anhydride tube, ...	0.0297
" titration, ...	0.0130
	9.0293
Reduction to vacuum, ...	45
	9.0338
Tare of balloon and gas, ...	11.5907
	2.5569
Tare of empty balloon, ...	
Value by Regnault's method, ...	2.5573

The value of the tare of the empty balloon found by the new chemical method is directly comparable with that obtained by the Regnault method, since there was no change in the balloon meanwhile. But after this determination was finished, the balloon, as it remained standing in its case, having been exposed to the direct sunshine of an unusually hot June day, some of the cerate lubricating the stop-cocks melted and ran down into the tubulatures below, from which it had to be removed. Thus the tare was lessened by nearly a centigram. It was easy, however, to determine the exact loss, and as in a like investigation, even when using the greatest care, one must ever be liable to accidents of this sort, it is important to dwell on this point.

In losing the tare we had apparently lost the thread of our investigation, but we were readily able to recover this thread without interrupting the general course of the work. It must be borne in mind that our immediate object was to obtain by the chemical method a series of results for the tare of the empty globe which could be compared with the mean value 2.5573 obtained by the method of Regnault. Here had come a change of tare, and we could obviously find a new standard of comparison by redetermining the new value by the old method. But this was not necessary. In the first determination by the chemical method, we had observed with great precision the pressure and temperature at which the balloon was filled. We do the same in the second determination, to which we next proceed, although these values are not needed in this determination, by itself considered, any more than they were in the first. If now from the tare of balloon and gas in the first determination (11.5907) we deduct 2.5573, we have the weight of carbonic acid which the balloon contains at a known temperature and pressure as found by the method of Regnault. If we deduct the same quantity from the tare found in the second determination, we have the weight of gas which the balloon holds at another temperature and pressure by the same method. If now there has been no change of tare, these two weights ought to agree exactly when one is reduced to what it would have been under the conditions at which the other was taken; and if there has been a change of tare, the difference of the weights thus reduced will give the exact amount of the loss, on the basis solely, let it be noticed, of results obtained after the method of Regnault. Thus we have:

By No. 1, weight of CO ₂ at 763.85 mm. and 25.08°	Grams. 9.0273
" No. 2, " " 756.73 " " 22.40°	9.0334
Weight No. 1 reduced at " " " "	9.0241

Loss of tare, 9.3 mg.

Obviously the accuracy of this result depends upon the accuracy with which the observations of temperature and pressure were made, and upon the correctness of the data on which the reductions are based. That the accuracy is extreme will appear from a comparison of the values of the specific gravity of carbonic acid, given on page 537, which were deduced from the same elements. And although in such work as this there is an obvious liability to error from just such a change of tare as we have been discussing, yet the loss or gain thus resulting is usually of such a magnitude that it cannot be overlooked.

Besides the one of which the details have been given, we made by the chemical method two other determinations of the tare of the empty globe in precisely the same manner as before described, and obtained the values 2.5481 and 2.5475 respectively. In order to bring these results into comparison with that obtained by the first determination, or those obtained by the method of Regnault, we must add 9.3 mg. to each value. We then have for

Tare of Empty Balloon.

	Regnault's Method.	Chemical Method.
No. 1,	2.5573	2.5569
No. 2,	2.5572	2.5574
No. 3,	2.5574	2.5568
Average,	2.55730	2.55703

These results are essentially identical, and the two methods confirm each other. But having reached this important conclusion, which was the main object of our investigation, we freely concede the preference to Regnault's method. The difference between the results of the two methods, as here exhibited, is insignificant; but so long as the validity and value of the correction for the contraction of the balloon on exhaustion has been thus established, Regnault's method will be preferred, because it is practically more simple, and hence the results are more accordant

than those obtained by the chemical method first described in this paper.

During the course of our investigation there were two marked changes in the tare of our balloon. One of these has been described. The other arose from the circumstance that the thin paraffine (vaseline) which was most suitable for lubricating the stop-cocks during the winter, no longer kept the joints tight when the heat of approaching summer rendered the material more liquid; and it became necessary to remove the stoppers and re-lubricate them, and it was the excess of cerate then used which melted and ran into the tubulatures subsequently.

There are then three separate values of the tare of the empty balloon to be used in our further calculations, all determined by or dependent upon Regnault's method, and all known with equal accuracy. These values we shall distinguish by the letters A, B and C, and we shall designate by the same letters the experimental data or calculated results into which these values enter as elements.

Tare of Empty Balloon.

Values.	
A	2.5098 grams.
B	2.5573 "
C	2.5480 "

Density of Air freed from Moisture and Carbonic Acid.

In these determinations the balloon was placed in the calorimeter case and connected with the Bunsen pump through an overflow jar. Air was then drawn into it through the purifiers we have described, and the reflux current which followed for a moment when the inlet cock was closed was supplied from the previous overflow. In other respects the determinations were made as before described, and we obtained the following data for the weight of air held in the balloon at different temperatures and pressures.

Summary of Air Weights.

A	No. 1,	weight of air at 762.63 mm. and 18°.52	= 6.0347 grams.
A	" 2,	" " 758.71 " "	19°.96 = 5.9745 "
B	" 1,	" " 750.30 " "	23°.32 = 5.8411 "

Reducing now these weights to what they would have been at

the temperatures and pressures we have assumed as standards, we obtain the following comparable values :

Reduced Air Weights for

$$\begin{aligned} H &= 761.99 \text{ mm.} = 300 \text{ d. in.}^1 \text{ and} \\ T &= 27^\circ \text{ C.} = 300^\circ \text{ absolute temperature.} \end{aligned}$$

A No. 1	5.8584 grams.
A " 2	5.8588 "
B " 1	5.8586 "

$$\text{Average value,} \quad 5.8586 \text{ grams.}^2$$

Density of Hydrogen.

We have for the weight of hydrogen held by the balloon the following data :

B No. 1,	weight hydrogen at 763.10 mm. and $21^\circ.08 = 0.4164$ gram.
B " 2, " " " "	" 764.92 " " $20^\circ.52 = 0.4178$ "
B " 3, " " " "	" 758.96 " " $22^\circ.75 = 0.4123$ "

¹ We shall use the abbreviation d. in. for tenths of an inch, after the analogy of d. m. for tenths of a meter.

² In the calculations of density and specific gravity, a still further, although wholly unimportant, correction has been made for the buoyancy of the air on the *brass* weights used to complete the tare in weighing the balloon, and in this connection it must be borne in mind that the *platinum* or *aluminum* fractions of a gram in a set of weights have always been adjusted to the larger *brass* weights in the air, and are therefore the equivalent of *brass* weights of the same denominations. The volume of the counterpoise was adjusted when the balloon was full of air; but although the compensation may be perfect through all ordinary changes of temperature and pressure, it cannot be regarded as absolute. In a laboratory, such changes seldom amount in the aggregate to more than the equivalent of one twentieth of the normal atmospheric pressure; and although such a variation might not produce a sensible effect on the apparent weight of the small amount of brass used in our weighings, twenty times this effect, which we should have if the brass weights were wholly uncompensated, might be an appreciable quantity. In weighing the balloon the largest amount of brass weights used was about 21.5 grams, which at 300 d. in. and 27° C. displace 1.6 mg. of air. One twentieth of this value would be barely, if at all, perceptible, but the whole quantity might cause a serious error in our results.

The tare of the empty balloon as first found by Regnault's method was 2.5573 grams; and we must assume that in the system consisting of balloon counterpoise and weights there may be outstanding a very small uncompensated volume, so that the true tare would be represented by

$$W_R = 2.5573 \pm w.$$

We next find the weight of the balloon filled with hydrogen gas, and it is obvious that under standard conditions the true weight, or

$$W' = 2.5573 \pm w + 0.4076 - w',$$

where w' represents the buoyancy of air on 0.4076 gram of brass. So the true weight of the balloon filled with air must be

$$W'' = 2.5573 \pm w + 5.8594 - w'',$$

Reduced Weights.

$$H = 300 \text{ d. in. } T = 27^{\circ} \text{ C.}$$

B No. 1,	0.4076
B No. 2,	0.4072
B No. 3,	0.4081

Average,	0.4076
----------	--------

Specific Gravity of Hydrogen.

$$\text{Air} = 1.$$

The values were obtained by dividing each of the weights of hydrogen above given by the average weight of air (5.8586), after reduction for the temperatures and pressures at which the hydrogen weights were observed. The calculations were verified by dividing each of the reduced weights of hydrogen by the average reduced weight of air as above, and the same figures were obtained in both ways.

B No. 1,	.	.	.	.	.	.	0.06957
B No. 2,	.	.	.	.	.	.	0.06951
B No. 3,	.	.	.	.	.	.	0.06966
Average,	.	.	.	.	.	.	0.06958
Average, using values of tare by chemical method,							0.06962

where w'' represents the buoyancy of air on 5.8594 grams of brass. In like manner, the true weight of the balloon filled with carbonic acid gas is

$$W''' = 2.5573 \pm w + 8.9564 - w''',$$

where w''' is the buoyancy of air on 8.9564 grams of brass.

Taking 1.176 mg. as the weight of 1 cc. of air at 300 d. in. and 27° C. , the standard conditions to which the weights have been reduced, we have

$$w' = 0.05 \text{ mg.}, \quad w'' = 0.84 \text{ mg.}, \quad w''' = 1.28 \text{ mg.};$$

and further,

$$W' - W_R = 0.4076 - 0.00005 \text{ gram. True weight of hydrogen.}$$

$$W'' - W_R = 5.8594 - 0.00084 \text{ " " " " air.}$$

$$W''' - W_R = 8.9564 - 0.00128 \text{ " " " " carbonic acid.}$$

These corrections should be applied to the weights before calculating the specific gravities, although they only alter the last values one or two units in the last decimal place; and in this paper, as is usual, the decimals are carried out one figure beyond the limits of accuracy.

In the chemical method we also took the weight of the balloon filled with carbonic acid gas, and, as before, we have

$$W''' = 2.5573 \pm w + 8.9564 - w'''.$$

Then by chemical means we determined the absolute weight (*in vacuo*) of the carbonic acid which the vessel held, that is, the quantity represented by $8.9564 - w'''$. Subtracting this value from the total weight, we obtained the tare of the empty balloon by the chemical method, and this obviously is

$$W_0 = 2.5573 \pm w.$$

Thus, the buoyancy of the air on the weights is eliminated, and W_0 is directly comparable in all its relations with W_R .

Specific Gravity of Oxygen.

Hydrogen = 1.

In this investigation we have not made an additional determination of the specific gravity of oxygen gas referred to air, for the causes of error which are serious in the case of hydrogen are not appreciable when working with the heavier gas, and we cannot expect to improve on the results of Regnault. Assuming, then, for the specific gravity of oxygen gas referred to air the value 1.10562, as obtained by Regnault and corrected by Crafts, and dividing this value by each of the values for the specific gravity of hydrogen gas given above, we have the following values for the specific gravity of oxygen referred to hydrogen :

B No. 1,	.	.	.	.	.	15.892
B No. 2,	.	.	.	.	.	15.907
B No. 3,	.	.	.	.	.	15.873
Average,	.	.	.	.	.	15.891
Average of chemical method,	.	.	.	.	.	15.882
Value found by Lord Rayleigh,	.	.	.	.	.	15.884

Density of Carbonic Acid.

For the weight of carbonic acid gas held in the balloon at different temperatures and pressures we have the following data :

B No. 1,	weight of CO ₂ at 756.73 mm. and 22°.40	9.0334 grams.
C No. 1,	" " 760.50 " " 25°.56	8.9821 "
C No. 2,	" " 759.13 " " 26°.60	8.9348 "

Taking now the average value of the weight of air held in the balloon at 300 d. in. = 761.99 mm. and 27° (viz. 5.8586 grams), and reducing this weight to what it would have been under the condition at which each of the four weights just given was observed, and then dividing each of these weights (corrected as by previous note) by the weight of air under the same conditions, we obtain the following results :

Specific Gravity of Carbonic Acid. Air = 1.

	Wt. of CO ₂ .	Wt. of Air.	II.	T.	Sp. Gr.
B No. 1,	9.0321	5.9088	756.73	22°.40	1.52858
C No. 1,	8.9808	5.8753	760.50	25°.56	1.52855
C No. 2,	8.9335	5.8445	759.13	26°.60	1.52855
Average value,	.	.	.	.	1.52856
Average value by chemical process,	.	.	.	.	1.52854

Taking lastly the average value of the weight of hydrogen held in the balloon at 761.99 mm. and 27° (viz. 0.4076 gram), and dividing the several weights of carbonic acid by this weight reduced to the same conditions, we have,—

Specific Gravity of Carbonic Acid. Hydrogen = 1.

	Wt. of CO_2 .	Wt. of H_2 .	H.	T.	Sp. Gr.
B No. 1,	9.0321	0.4111	756.73	$22^{\circ}.40$	21.971
C No. 1,	8.9808	0.4088	760.50	$25^{\circ}.56$	21.971
C No. 2,	8.9335	0.4066	759.13	$26^{\circ}.60$	21.971
Average value, ...					21.971
Average value by chemical process, .					21.957

The close agreement, indeed the essential identity, of these results should be noticed, as this fully substantiates the extreme accuracy of the method of recovering the lost tare of the empty balloon described on page 532. It is true that, as the values of the specific gravity of carbonic acid have been calculated with an average value of the several reduced weights of hydrogen or air, an error in these data would not affect the results; but any error in the observed weights of carbonic acid would appear to its full extent.

Moreover, the striking fact should not be overlooked that the specific gravity of carbonic acid gas referred to hydrogen approaches much more nearly 22, the half molecular weight of carbonic acid gas as generally assumed, than does that of oxygen gas when referred to the same standard, the corresponding whole number 16, and the significance of the circumstance is obvious. If we assume that the atomic weight of oxygen, as determined by Dr. Richards under my direction, is 15.87,¹ then the corresponding atomic weight of carbon would be 11.90, and the half molecular weight of carbonic acid 21.82. Theoretically, this number ought also to define the specific gravity of carbonic acid gas referred to hydrogen gas, if the two gases were compared under the same conditions of high temperature and indefinite expansion. But under the great pressure of our atmosphere the molecular volume of carbonic acid gas is known to be condensed to a measurably greater degree than the potentially equal molecular volume of hydrogen gas, and the result must be a proportionally increased

¹ This Journal 10, 194 (1888); and Proceedings Am. Acad. 23, 185 (1888).

density; and, moreover, the inequality in the condensation of the two gases must be increased by the circumstance that at the ordinary temperature of the air carbonic acid gas is below the critical point, while hydrogen gas is very far above it. If, however, this is true in the case of carbonic acid gas, our knowledge of the deviations from Mariotte's law compels us to infer that the same must be true in some small measure, although in a much less degree, in the case of oxygen gas; and it would lead us to expect that the specific gravity of oxygen gas referred to hydrogen gas would be slightly greater, certainly not less, than the corresponding half molecular weight. Now we have from the results published in this and our preceding paper:

Half molecular weight of carbonic acid gas, ...	21.82
Sp. gr. of carbonic acid gas (referred to hydrogen gas),	21.96
Half molecular or atomic weight of oxygen gas, . . .	15.87
Sp. gr. of oxygen gas (referred to hydrogen gas), . .	15.88

It has been thought to discredit the low value of the atomic weight of oxygen we have found by the very easy but wholly gratuitous assumption that the hydrogen gas on which we experimented was impure, and we had intended in this investigation to demonstrate the identity of the gas from the several sources employed by a comparison of their specific gravities. We are under great obligations to Lord Rayleigh, who has relieved us from this necessity by anticipating the work. He has experimented on hydrogen gas, not only from all the sources we used, but also on gas which had been occluded by palladium, and has obtained the same result in all cases; namely, the value 15.884,¹ essentially identical with that which we have found in this investigation with the hydrogen gas from our electrolytic apparatus.²

This point, however, had not been overlooked in the previous paper. It was there shown that the results obtained, in *three distinct series of experiments*, with hydrogen gas prepared by *three different processes* and with *three different forms of apparatus*, were essentially identical.³ On the doctrine of chances, such an agreement would have been practically impossible had there been an appreciable amount of accidental impurities in the gas from

¹ Proceedings of the Royal Society 45, 425.

² This Journal 10, 102 (1888); and Proceedings Am. Acad. 23, 168 (1888).

³ See table, this Journal 10, 107 (1888); and Proceedings Am. Acad. 23, 173 (1888).

either of the sources. We say accidental impurities, for there may be inherent impurities common to the gas from all sources, of which we as yet know nothing; and, as we wrote before, "The question still remains, Is the hydrogen gas thus prepared the typical hydrogen element? But this is the same question which must arise in regard to any one of the elementary substances; and all that we can say is, that the evidence in regard to the purity of the hydrogen we have used is as good as any that can be adduced in regard to any one of the elementary substances whose atomic weight has been most accurately determined."¹

It is not to be expected that our results, or those of our contemporaries, are final. The most that has been accomplished by recent investigation is to show that the ratio of the atomic weight of oxygen to that of hydrogen, deduced from the elementary substances, as we know them in their purest condition, is decidedly less than that of 16 to 1. The evidence as to the exact value of this ratio is still conflicting, and although after our experience we cannot see how greater accuracy could be gained by any variation of our process, we are far from claiming that our results have not been vitiated by unknown constant errors. Fortunately, an exact knowledge of the ratio is at present of no practical importance in chemical analysis. The only question on which the actual small indefiniteness has a bearing is the unit of atomic weights, a question that has been much discussed of late; but here, as it seems to us, one consideration should be conclusive.

Every one who has worked on the oxygen and hydrogen ratio knows that the resources of experimental science have been taxed to the utmost in these investigations. Greater accuracy is not to be expected with our present appliances, and yet there is an outstanding uncertainty amounting to more than one-half of one per cent. of the value. This corresponds to a variation of more than one unit in many of the higher atomic weights; and unless we are willing that these *chemical constants* should fluctuate to this extent with every new determination of the fundamental ratio, we must seek a more invariable basis. The most natural and stable unit is the atomic weight of oxygen, not only on account of the wonderful combining power of this element, but also because the ratio of the combining weights of most of the elements to that of oxygen are known with great precision; and many cogent reasons could be

¹ This Journal 10, 108 (1888); and Proceedings Am. Acad. 23, 174 (1888).

PLATE I.

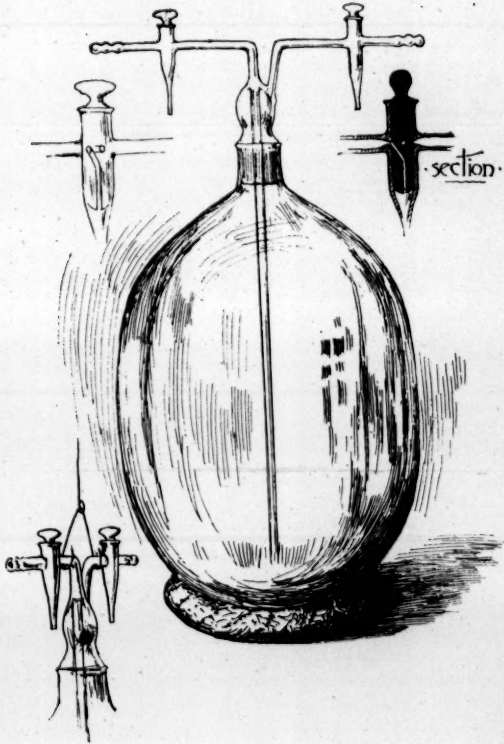


PLATE II.

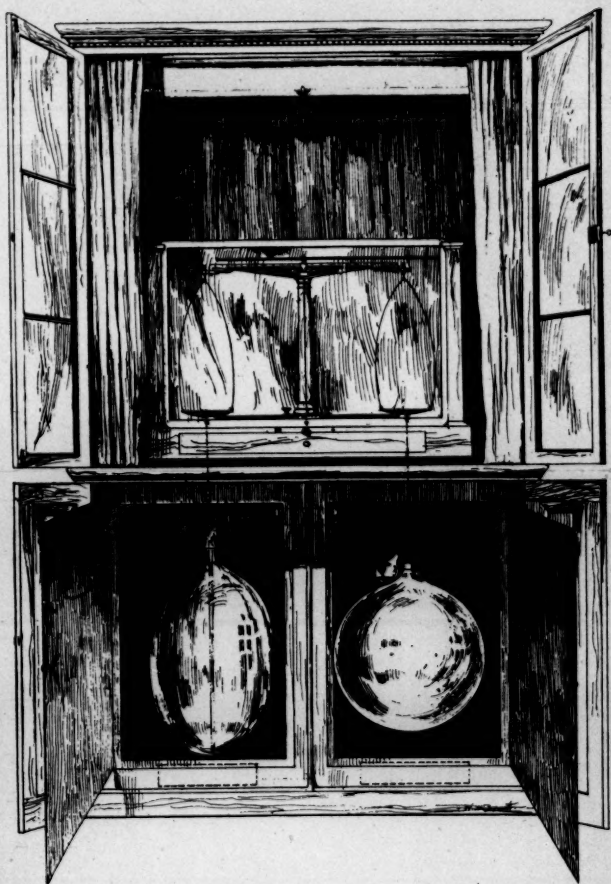
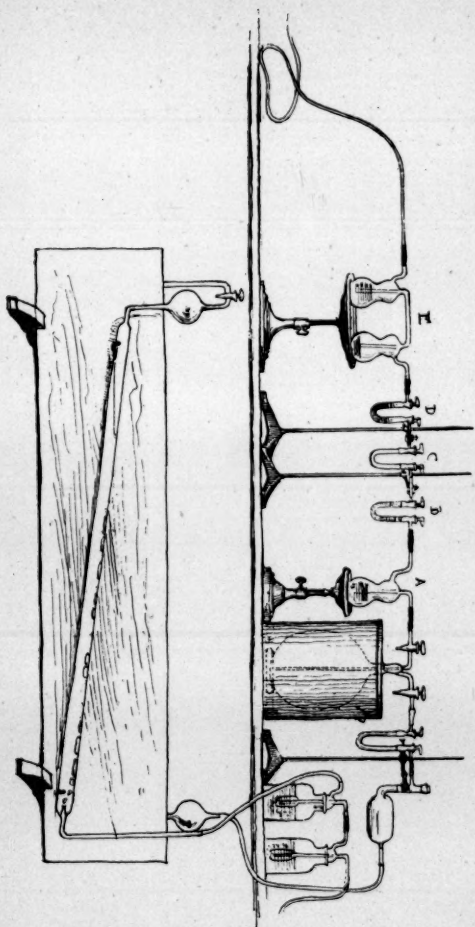


PLATE III.



urged for returning to the system of Berzelius, which referred all the other weights to that of oxygen, assumed to be 100. But this system would not exhibit to advantage the numerical ratios on which modern chemical classification is based. Hence for a provisional system we most warmly approve of that which assumes $O = 16$ as its basis, and of the best-known atomic weights leaves only the value of H to vary with our changing knowledge. This system has all the stability it is possible at present to secure, and exhibits to advantage the relations which are important in classification. Moreover, it is no small recommendation to this system that a large number of the weights are whole numbers, within the limits of error of ordinary analytical work, and for this reason can be easily remembered.

In conclusion, I would express my obligations to my nephew, Dr. Oliver W. Huntington, for the great aid he has given throughout this investigation. With the help of his skill in glass-blowing I have been able to secure all the connections of my gas generators with melted or cement joints, except the direct connections with the globe, where india-rubber could not be avoided. He has also constantly assisted my impaired eyesight in the observations with barometer and thermometer on which the accuracy of the work greatly depended. I have likewise been indebted to Dr. Arthur M. Comey for making the titrations required, and to Mr. W. W. Bosworth for the drawings with which this paper is illustrated.

LXV.—ON THE ACTION OF SODIUM MALONIC ESTER ON TRIBROMDINITROBENZOL.

SECOND PAPER.

BY C. LORING JACKSON AND W. S. ROBINSON.¹

In a previous paper² on this subject we were obliged to publish several results in an unfinished condition, because at the time we saw no chance of being able to continue the work together. Since then, however, unforeseen circumstances have allowed us to go on with the research, and in this paper we describe work which fills up most of the gaps in our former publication.

¹ From the Proceedings of the American Academy of Arts and Sciences, communicated by the authors.

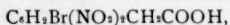
² This Journal 11, 93 (1889).

The most important results contained in this paper may be stated briefly as follows. The reactions by which the bromdinitrophenylmalonic ester is formed have been made out to be the following :

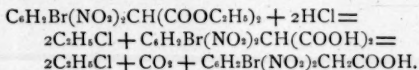
- I. $\text{C}_6\text{HBr}_2(\text{NO}_2)_2 + \text{CHNa}(\text{COOC}_2\text{H}_5)_2 =$
 $\text{NaBr} + \text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CH}(\text{COOC}_2\text{H}_5)_2.$
- II. $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CH}(\text{COOC}_2\text{H}_5)_2 + \text{CHNa}(\text{COOC}_2\text{H}_5)_2 =$
 $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CH}_2(\text{COOC}_2\text{H}_5)_2.$
- III. $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CH}_2(\text{COOC}_2\text{H}_5)_2 =$
 $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CHBr}(\text{COOC}_2\text{H}_5)_2.$
- IV. $\text{CHNa}(\text{COOC}_2\text{H}_5)_2 + \text{H}_2\text{O} = \text{NaOH} + \text{CH}_2(\text{COOC}_2\text{H}_5)_2.$
- V. $\text{CHBr}(\text{COOC}_2\text{H}_5)_2 + \text{NaOH} = \text{NaBr} + \text{CHOH}(\text{COOC}_2\text{H}_5)_2.$

The proof of these reactions consisted in the isolation of tartronic acid from the mixture obtained by the saponification of the oily secondary product with hydrochloric acid.

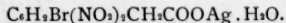
The action of concentrated hydrochloric acid, or, better, sulphuric acid of specific gravity 1.44, upon the bromdinitrophenylmalonic ester has been studied, and we are able to correct some of the preliminary statements made on this subject in our first paper. The product is the bromdinitrophenylacetic acid



which melts at 177° , and is formed, when hydrochloric acid is used, by the following reactions:



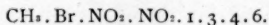
The crystalline silver salt of this acid was analysed, and proved to have the formula



With sodic hydrate a deep Prussian green or with an excess a yellowish brown solution is formed, from which acids throw down a pale crimson precipitate, or a white one which becomes pale crimson when moistened with alcohol; none of these substances could be brought into a state fit for analysis, but we found that bromine was removed in their formation.

The bromdinitrophenylacetic acid is broken up when boiled with alcohol into bromdinitrotoluol and carbonic dioxide; boiling

with water produces the same effect, but much more slowly. A few drops of sulphuric acid prevent the decomposition by boiling water. This conversion into bromdinitrotoluol gave us the means of determining the constitution of the bromdinitrophenylmalonic ester and its derivatives; as Messrs. W. B. Bentley and W. H. Warren have, at our request, worked out the constitution of the substituted toluol, and found that it is as follows:



It follows, therefore, that all the substances mentioned in this and our former paper must have a similar constitution, and that in making the bromdinitrophenylmalonic ester from tribromdinitrobenzol the bromine atom replaced by the malonic radical is one of those which is at the same time para and ortho to the nitro groups, the one replaced by hydrogen is ortho to the two nitro groups, while the third atom of bromine, which remains unaltered, occupies exactly the same position as that replaced by the malonic ester radical—certainly a curious result.

Preparation of Bromdinitrophenylmalonic Ester.

Our longer experience in the preparation of bromdinitrophenylmalonic ester has led us to introduce several improvements into the process, which now we carry on as follows. A strong benzol solution of 20 grams of tribromdinitrobenzol (benzol is to be preferred to the ether used formerly, because the tribromdinitrobenzol is more soluble in it) is mixed with 16 grams of malonic ester, previously converted into sodium malonic ester by treatment with the sodic ethylate from 2.3 grams of sodium and about 100 to 125 cc. of alcohol, and the mixture allowed to stand over night at ordinary temperatures. The red solution thus obtained is treated with water, which separates it into two layers, a dark red aqueous solution containing the sodium salt of bromdinitrophenylmalonic ester and sodic bromide, and a benzol solution of the unaltered tribromdinitrobenzol with the oily product of the reaction. The two layers are separated with a drop-funnel, and the lower aqueous one acidified with dilute sulphuric acid; this throws down a yellowish white precipitate of the bromdinitrophenylmalonic ester, which is purified by crystallisation from hot alcohol, until it shows the constant melting point 76° .

In this way 20 grams of tribromdinitrobenzol gave 7.9 grams of

the bromdinitrophenylmalonic ester,¹ and 5.1 grams of tribromdinitrobenzol were recovered from the benzol solution. Subtracting this from the 20 grams there are left 14.9 grams of tribromdinitrobenzol which entered into the reaction, and should have given the same weight, 14.9 grams of the product, so that the yield was 53 per cent. of the theory, or about the same as that obtained by the process as given in our first paper, which calculated in the same way becomes 50 per cent.

In the course of some other experiments the curious observation was made that it is not necessary to use sodic ethylate to bring about the action of malonic ester on the tribromdinitrobenzol, as a little of the red salt of bromdinitrophenylmalonic ester was formed when *aqueous* sodic hydrate was added to a mixture of the two organic substances. This recalls the observation of Victor Meyer,² that homologues can be obtained from benzyl cyanide by using the alkylhaloid with powdered solid sodic hydrate instead of sodic ethylate, or from desoxybenzoin by the use of an alcoholic solution of an alkaline hydrate.

Study of the Reactions by which the Bromdinitrophenylmalonic Ester is formed.

One of the most important points, which want of time prevented us from considering in our first paper, was the mechanism of the reactions by which the bromdinitrophenylmalonic ester was formed from the tribromdinitrobenzol, and accordingly this was one of the first points to which we turned our attention in taking up the subject again. The reaction consists essentially, as our analyses of the product showed, in the replacement of one of the bromine atoms in the tribromdinitrobenzol by the malonic ester radical $\text{CH}(\text{COOC}_2\text{H}_5)_2$, and of a second by hydrogen forming $\text{C}_6\text{H}_4\text{Br}(\text{NO}_2)_2\text{CH}(\text{COOC}_2\text{H}_5)_2$, and the obscure part of it is the manner in which this second atom of bromine is replaced by hydrogen. The first step toward clearing up this obscurity was obviously to

¹ Dr. G. D. Moore, in his work with me on the action of sodium acetacetic ester on tribromdinitrobenzol, has found that a much better yield is obtained if the mixture is boiled for an hour under a return condenser. This observation was not made until the work described in this paper was finished and Mr. Robinson had left Cambridge, so that it was not convenient to try the experiment of boiling the solution of sodium malonic ester and tribromdinitrobenzol, nor did it seem very desirable to do so, as when we first took up the subject such an experiment was tried and seemed to yield very unfavorable results. I propose, however, to repeat the experiment next year, if I return to the study of these compounds.

C. L. J.

² Ber. d. chem. Ges. **21**, 1291 (1888).

make out whether this atom of bromine was eliminated in the form of some organic compound, or as sodic bromide, which was done by the following quantitative determinations of the amount of sodic bromide formed in the reaction.

I. 20 grams of tribromdinitrobenzol were treated with the sodium malonic ester from 16 grams of malonic ester in the way already described, and, after precipitating the bromdinitrophenylmalonic ester from the aqueous solution with dilute nitric acid, and filtering it out, the amount of sodic bromide was determined by precipitation of argentic bromide from an aliquot part of the filtrate, and calculating the amount in the entire solution. In this way the whole solution was found to yield 13.81 grams of argentic bromide, corresponding to 5.88 grams of bromine. The benzol solution on evaporation yielded 5.1 grams of tribromdinitrobenzol, which had not taken part in the reaction, leaving 14.9 grams which had acted, and which would yield 5.89 grams of bromine, if two of the atoms of bromine had been removed from each molecule as sodic bromide.

II. 20 grams of tribromdinitrobenzol gave under the same conditions 13.8 grams of argentic bromide, corresponding to 5.87 grams of bromine, but only 4.9 grams of tribromdinitrobenzol were recovered unaltered. The 15.1 grams of tribromdinitrobenzol which entered into the reaction should have lost 5.96 grams of bromine.

Percentage of the theoretical amount of bromine removed from tribromdinitrobenzol in the form of sodic bromide:

I.	II.
99.86	98.49

These numbers agree as closely as could be expected, when the necessary sources of error in the process are considered, and prove that all the bromine removed by the reaction is converted into sodic bromide.

The second point to be determined was from what source the atom of hydrogen was obtained which replaced the atom of bromine. For this purpose we investigated the oily product of the reaction, and, after we had found that nothing definite could be obtained from it by distillation under ordinary pressures, or with steam, and that sodic hydrate or other alkaline saponifying agents gave most unpromising results, we tried heating it with strong hydrochloric acid in a sealed tube to 130° for 20 hours, as

the bromdinitrophenylmalonic ester, which was dissolved in the oil, would be converted by this treatment into the corresponding phenylacetic acid, with the properties of which we were familiar, and which, therefore, we thought could be removed easily from the other products of the reaction. The tubes after heating contained an aqueous solution and a small amount of viscous matter, which gradually changed into an amorphous solid. These were separated by filtration, and the filtrate evaporated to dryness on the water-bath, leaving a crystalline residue, which was extracted with cold water to leave behind the bromdinitrophenylacetic acid present. The extract after being evaporated again on the water-bath gave crystals, which made up about one-half the amount of the residue from the first evaporation. They were freely soluble in water or alcohol, nearly insoluble in ether, and could be sublimed at temperatures below their melting point, forming glassy white thick needles or prisms, which melted at 185° . These properties proved that the crystals are tartronic acid, as they are identical with those given by Conrad and Bischoff for that substance.¹ We tried also to confirm this inference by an analysis, but the small amount of the acid which, after some unsuccessful experiments, remained at our disposal, little more than 0.1 gram, prevented us from purifying it thoroughly, as sublimation, which had given the substance melting at 185° , turned out to be too wasteful a process for working up large amounts; we were not surprised, therefore, that our analysis of the silver salt gave 62.82 per cent. of silver, instead of the 64.69 per cent. calculated for argentic tartronate. This result, however, bad as it is, comes nearer to that for argentic tartronate than to that for any other substance which could well be formed, and therefore gives us the desired confirmation.² The small amount of tartronic acid obtained, less than 0.5 gram from about 10 grams of the oil, may be accounted for on the supposition that the larger part of the tartronic acid was decomposed by the strong hydrochloric acid used in the saponification of the oil, as Conrad and Bischoff³ have observed that tartronic acid is decomposed very easily by hydrochloric acid, and we also were unable to obtain a trace of the acid

¹ Ann. Chem. (Liebig) 209, 222 (1881).

² No attempt was made to obtain a better analysis of the tartronic acid, because the work upon the corresponding trinitro compound described in another paper furnished a complete confirmation of the theory of the reactions given here.

³ Ann. Chem. (Liebig) 209, 223 (1881).

from the filtrate after argentic chloride had been precipitated from the silver salt by a slight excess of hydrochloric acid. In fact, we should not have thought it worth while to try to obtain tartronic acid by the action of hydrochloric acid on our oil, if it had not been for the fact that tartronic ester has been made from calcic tartronate by the action of hydrochloric acid gas and alcohol,¹ which would seem to show that the tartronic acid is more stable in presence of strong than of dilute hydrochloric acid, improbable as this sounds. This view is in harmony with our observations detailed above, and Conrad and Bischoff state that even very dilute acid decomposes it readily; but even granting this, a large proportion of the tartronic acid must have been decomposed during the treatment with hydrochloric acid, and this seems to us sufficient to make it more than probable that the tartronic acid is the product of the principal reaction, and not formed in a secondary one taking place only to a limited extent. If this is admitted, the following reactions would give the most probable explanation of what takes place:

- I. $\text{C}_6\text{HBr}_2(\text{NO}_2)_2 + \text{NaCH}(\text{COOC}_2\text{H}_5)_2 =$
 $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CH}(\text{COOC}_2\text{H}_5)_2 + \text{NaBr}.$
- II. $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CH}(\text{COOC}_2\text{H}_5)_2 + \text{NaCH}(\text{COOC}_2\text{H}_5)_2 =$
 $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CH}_2(\text{COOC}_2\text{H}_5)_2.$
- III. $\text{C}_6\text{HBr}_2(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CH}_2(\text{COOC}_2\text{H}_5)_2 =$
 $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{CNa}(\text{COOC}_2\text{H}_5)_2 + \text{CHBr}(\text{COOC}_2\text{H}_5)_2.$
- IV. $\text{NaCH}(\text{COOC}_2\text{H}_5)_2 + \text{H}_2\text{O} = \text{NaOH} + \text{CH}_2(\text{COOC}_2\text{H}_5)_2.$
- V. $\text{CHBr}(\text{COOC}_2\text{H}_5)_2 + \text{NaOH} = \text{CHOH}(\text{COOC}_2\text{H}_5)_2 + \text{NaBr}.$

Of these reactions, I, II, and III take place before, IV and V after, the addition of the water used in working up the product. That Reaction III takes place we infer from our discovery of tartronic acid among the products of saponification of the oil, as Conrad and Bischoff² have proved that brommalonic ester is decomposed by sodic hydrate, according to Reaction V.³

The experiments of one of us with G. D. Moore upon the action of sodium malonic ester on tribromtrinitrobenzol have shown that these reactions take place in a way analogous to that

¹ Freund, Ber. d. chem. Gesell. **17**, 786 (1884). Pinner, *ibid.* **18**, 757 (1885).

² Ann. Chem. (Liebig) **209**, 222 (1881).

³ A fuller discussion of these reactions will be found in the general paper at the end of this series.

just worked out. For the details we would refer to the paper on this subject.

The objection which might be raised against these reactions, that the yield of bromdinitrophenylmalonic ester is at best only about 50 per cent. of that required by theory, and therefore that some other substance may be formed from the tribromdinitrobenzol in addition to it, is disposed of by the fact that on making the dibromdinitrophenylmalonic ester from tetrabromdinitrobenzol by exactly analogous reactions, the yield rose to 80 per cent. of the theoretical. It follows, therefore, that the 47 to 50 per cent. unaccounted for in our preparations remained dissolved in the oily secondary product; but although we have made many attempts to recover it, none of them have been crowned with success.

Saponification of Bromdinitrophenylmalonic Ester.

In our previous paper we stated that strong hydrochloric acid decomposed bromdinitrophenylmalonic ester, when the two substances were heated together to 140° – 145° in a sealed tube, and described the product formed, stating, however, that all our results up to that time must be regarded as preliminary. Upon taking up the subject again, we studied in the first place the gas evolved when the tube was opened, and found that, in addition to the gas already mentioned burning with a green-bordered flame (which is undoubtedly ethyl chloride), carbonic dioxide was given off, as was proved by the precipitate formed when the gas was passed through lime-water. It is to be observed, however, that if the temperature to which the tubes were heated was 140° , or a little lower, very little, if any, carbonic dioxide was given off, and the product insoluble in the hydrochloric acid was oily; on the other hand, when a crystalline product was obtained at a somewhat higher temperature, carbonic dioxide was given off freely. We next attempted to prepare the substance in open vessels by substituting for strong hydrochloric acid dilute sulphuric acid boiling at about the temperature to which we heated the tubes, and found that not only did we obtain the product in this way, but that it was much purer than that made in the sealed tubes with hydrochloric acid. We have arrived accordingly at the following method as the most convenient for saponifying the bromdinitrophenylmalonic ester. 2 grams of the ester are mixed with

about 100 cc. of dilute sulphuric acid, specific gravity 1.44 and boiling point 132° , and the mixture boiled in a flask with a return condenser, until the oily drops of melted bromdinitrophenylmalonic ester have all gone into solution, which usually takes about an hour and a half. After this the solution, as it cools, deposits long, pale yellow needles of the new substance, which, if the preparation has succeeded well, melt at 177° at once. If, however, the action has not run so well, and the melting point is somewhat lower than this, the substance can be easily purified by crystallisation from boiling water acidified with a few drops of dilute sulphuric acid, but in no case should it be crystallised from pure water, or alcohol, as these solvents decompose it in the curious way described later in this paper, when we consider its properties.

Metabromdinitrophenylacetic Acid, $C_6H_4Br(NO_2)_2CH_2COOH$.

The substance prepared in the manner just described, and showing the constant melting point 177° , was dried at 100° , and analysed with the following results:

I. 0.2106 gram of the substance gave on combustion 0.2426 gram of carbonic dioxide and 0.0420 gram of water.

II. 0.1933 gram of the substance gave 15.6 cc. of nitrogen at a temperature of $15^{\circ}.5$ and a pressure of 759.2 mm.

III. 0.1821 gram of the substance gave, according to the method of Carius, 0.1152 gram of argentic bromide.

	Calculated for $C_6H_4Br(NO_2)_2CH_2CO_2H$.	I.	Found. II.	III.
Carbon	31.47	31.43		
Hydrogen	1.64	2.21		
Nitrogen	9.18		9.42	
Bromine	26.23			26.93

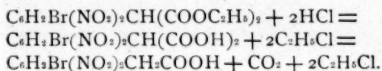
These analyses supersede those already published,¹ which were made with a substance prepared by crystallisation from dilute alcohol, before we had found that this solvent decomposed the compound; it was therefore decidedly impure, as indeed was shown by its melting point, which was 170° instead of 177° .

The yield of the bromdinitrophenylacetic acid is essentially quantitative, as two grams of the bromdinitrophenylmalonic ester gave, after treatment with dilute sulphuric acid, 1.4 grams of

¹ Proceedings Am. Acad., 24, 11 (1889).

bromdinitrophenylacetic acid melting at 177° , instead of the calculated amount, 1.56 grams, that is, 90 per cent. of the theory; the missing 10 per cent. without doubt remained dissolved in the dilute sulphuric acid, in which the substituted acetic acid is not wholly insoluble, as the 1.4 grams were obtained by simple filtration, no attempt being made to recover the organic substance from the filtrate.

In view of the observations described above, there can be no doubt that the following reactions take place when bromdinitrophenylmalonic ester is saponified by heating it with hydrochloric acid at temperatures in the neighborhood of 145° :



And there can be no question that a similar reaction takes place when dilute sulphuric acid is substituted for strong hydrochloric acid. In fact, this was so obvious that we have not thought it worth while to try to isolate the sulphovinic acid which must be formed in this case instead of the ethylchloride.

Properties.—The metabromdinitrophenylacetic acid crystallises from an aqueous solution containing a little sulphuric acid in yellowish white needles, often one or two centimeters long, which appear under the microscope as tolerably thick prisms frequently tapering owing to modification by the planes of a pyramid with a very acute angle, but almost always, even in addition to this tapering, terminated bluntly by the planes of another very obtuse pyramid. Occasionally the termination is a single plane at a moderately acute angle to the sides, but this looked as if it were due to cleavage. The crystals are generally very well developed, but if they are small, a tendency to twin longitudinally is observed. If the substance is crystallised from alcohol, the forms like feathers, or half-feathers, described in our previous paper, and groups of branching needles looking like certain feathery seaweeds, appear; but as the alcohol decomposes the substance, these forms can hardly be ascribed to the substituted acetic acid itself. It melts at 177° , and is essentially insoluble in ligroine or carbonic disulphide; very slightly soluble in chloroform, slightly in benzol, more soluble in both of these solvents when hot; tolerably soluble in ether, separating from the solution in a liquid form, which solidifies on

stirring; easily soluble in acetone or glacial acetic acid; soluble in cold alcohol, more freely in hot, but the alcohol decomposes it, as is indicated by the change in the appearance of the crystals, the long yellowish prisms of unaltered bromdinitrophenylacetic acid becoming roughly studded with fine needles of another substance, and by the lowering of the melting point, when the substance is crystallised from alcohol; evaporation to dryness of the alcoholic solution, if repeated three times, reducing the melting point from 177° to 147° ; while after two more evaporations, making five in all, the melting point had sunk to 103° – 104° , at which point it remained constant after repeated crystallisation. The substance obtained in this way crystallised in rectangular prisms, or plates, was not acted on by alkalies, and was recognised as Grete's metabromdinitrotoluol.¹ For greater certainty it was analysed, with the following results:

I. 0.1690 gram of the substance gave, by the method of Carius, 0.1210 gram of argentic bromide.

II. 0.2185 gram of the substance gave 20.3 cc. of nitrogen at a temperature of 22° .5 and a pressure of 773.3 mm.

	Calculated for $C_8H_5Br(NO_2)_2CH_3$.	I.	Found.	II.
Bromine	30.65	30.47		
Nitrogen	10.73			10.69

This conversion of the metabromdinitrophenylacetic acid into the corresponding toluol by boiling with alcohol, when it is so stable in presence of boiling dilute sulphuric acid, seemed to us so interesting that we have examined it more carefully. Having in the first place determined that the alcohol was neutral to test papers, to prove that the reaction could not be due to a trace of alkali, or acid in it, a quantity of the substance melting at 177° was boiled in a flask under a return condenser with a little alcohol for three hours, and pure air occasionally drawn through the apparatus to sweep out its contents into a set of absorption bulbs filled with lime-water; in this way a heavy precipitate was obtained, which consisted in great part of calcic hydrate precipitated by the alcohol vapor, but also contained calcic carbonate, as was shown by effervescence when it was dissolved in an acid, thus proving that carbonic dioxide had been given off. The alcoholic solution,

¹ Ann. Chem. (Liebig) **177**, 258 (1875).

after it had been boiled for an hour and a half longer, gave crystals, melting at 103° to 104° . It seems evident, therefore, that the reaction runs as follows:



and the alcohol seems to take no part in it. Methyl alcohol, in which the substance is more soluble than in ethyl alcohol, brings about a similar decomposition, but more slowly. In boiling water the metabromdinitrophenylacetic acid is tolerably soluble, but nearly insoluble in cold water. The decomposition produced by alcohol also takes place when the aqueous solution is boiled, but very slowly, so that long boiling is necessary to convert the substance completely into the substituted toluol; nevertheless, after distilling with steam for several hours, the whole of the substance had passed over into the receiver as metabromdinitrotoluol, since none of the substituted acetic acid, which does not distill with steam, was left in the flask. The presence of a very small amount of sulphuric acid (two or three drops of the dilute acid to 100 cc. of water) is sufficient to prevent this decomposition entirely, as a specimen of the substituted acetic acid showed no signs of decomposition, even after having been distilled with steam for three hours with only the amount of dilute sulphuric acid which remained adhering to it after the excess of acid used in its preparation had been removed by filtration. The best solvent for the bromdinitrophenylacetic acid, therefore, is boiling water containing a few drops of sulphuric acid. If the substance has become contaminated with the substituted toluol, it can be purified conveniently by distillation with steam in presence of a few drops of sulphuric acid, when the toluol passes over, and the acetic acid remains behind in the flask.

Ammonic hydrate dissolves the metabromdinitrophenylacetic acid, forming a colorless solution if the acid is in excess; but if the ammonic hydrate is added in slight excess, a green solution is obtained, which turns dark brown if a large excess of ammonic hydrate is added, but regains its green color on dilution with water. Both the colorless and green solutions smell of ammonia, and this smell could not be removed by gentle boiling, or by allowing the solution to stand over sulphuric acid, from which we infer that the ammonium salt is a decidedly unstable substance. When either solution is warmed on the water-bath for some time

it is partially decomposed with formation of a precipitate of metabromdinitrotoluol, and the green solution turns yellow even when allowed to evaporate spontaneously. Hydrochloric acid threw down from the solution a precipitate of metabromdinitrophenylacetic acid. The ammoniacal solution, prepared with an excess of the acid and freed as completely as possible from an excess of ammonia, gave no precipitate with baric, strontic, or calcic chloride, but with the salts of many of the heavy metals it gave precipitates, of which the following were the most characteristic:

Aluminic chloride, heavy, white.

Ferric chloride, heavy, very pale buff.

Cupric sulphate, heavy, pale blue.

Mercuric nitrate, heavy, yellowish white.

Mercuric chloride, a very slight precipitate, probably white precipitate from the slight excess of ammonic hydrate.

Mercurous nitrate, heavy, white.

Plumbic acetate, heavy, white.

Argentie nitrate, heavy, white.

The behavior with argentic nitrate is especially characteristic; if the solutions are strong, the mixture becomes nearly solid from the formation of a white flocculent precipitate, which frequently swells up, forming a little heap or pyramid, and after standing for some hours becomes converted into good-sized crystals. The analysis and properties of this salt are described more in detail below.

With sodic hydrate a solution of the acid turns a deep Prussian green color, which passes in time into a yellowish brown, this latter color appearing at once when an excess of sodic hydrate is added. If the green solution is acidified, a precipitate is obtained, which, although nearly colorless when dry, becomes purple when moistened with alcohol. This precipitate was oily at first, and, although it solidified later, we did not succeed in finding any solvent from which it could be crystallised. That the sodic hydrate had acted on the bromine was shown by an actual experiment, which gave the following results:

0.67 gram of the acid yielded by treatment with sodic hydrate so as to form the green salt, 0.1136 gram of argentic bromide, which corresponds to 0.0483 gram of bromine instead of the 0.1757 gram contained in the amount of acid taken; that is, 27.5 per cent. of the whole had been removed.

The yellowish brown solution obtained, when a large excess of

sodic hydrate was used, or the mixture of sodic hydrate and metabromdinitrophenylacetic acid was boiled for some time, gave on addition of an acid a viscous red substance, which was exceedingly unmanageable. That bromine was removed in quantity in this way is shown by the following determination:

0.2412 gram of the metabromdinitrophenylacetic acid was boiled with sodic hydrate for three-quarters of an hour; the product, after acidifying with nitric acid, and filtering out the precipitate, gave 0.1180 gram of argentic bromide, corresponding to 0.0502 gram of bromine instead of the 0.0632 gram contained in the weight of acid taken; that is, 79.4 per cent. of the whole.

It is evident, therefore, that the original compound has undergone a deep-seated alteration, and the new crimson substance is probably a phenol. This view of its nature receives some confirmation from the fact that it is decomposed with the greatest ease by even somewhat dilute nitric acid. We have not yet succeeded in bringing either of the products derived from sodic hydrate into a state fit for analysis, although the slight solubility of the barium salt of the crimson acid awakened hopes of success; but these ended in disappointment, as the salt proved quite as viscous as the free acid.

Potassic carbonate gives with the metabromdinitrophenylacetic acid results similar to those obtained with sodic hydrate, but less marked.

We hoped to be able to throw some light on this action of alkalis on the metabromdinitrophenylacetic acid by the study of the corresponding anilido compound, but have not succeeded as yet in preparing it, as aniline converts the free acid direct into metanilidodinitrotoluol,¹ $C_6H_5CH_2(C_6H_5NH)(NO_2)_2$, melting point 142° , and the saponification of anilidodinitrophenylmalonic ester with sulphuric acid yielded only uninviting viscous products.

Radziszewski,² Gabriel and R. Meyer,³ and Heckmann,⁴ have prepared a dinitrophenylacetic acid which differs from that just described only in containing no bromine. This substance also loses carbonic dioxide easily, passing into dinitrotoluol, but none of the chemists who have worked with it describe a decomposition by solvents similar to that observed by us; in fact, they crystallised it for analysis from boiling water, but, as in all their methods of preparation acids were used, it is possible that a sufficient

¹ Hepp, *Ann. Chem. (Liebig)* **215**, 371 (1882).

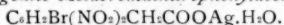
² *Ibid.* **14**, 823 (1818).

³ *Ber. d. chem. Gesell.* **2**, 210 (1869).

⁴ *Ann. Chem. (Liebig)* **220**, 134 (1883).

amount of sulphuric acid was present during the crystallisation to prevent the decomposition. It appears that none of them tried to crystallise it from alcohol. The statement is made, however, that the sodium or potassium salt of the acid decomposes slowly on standing, instantly on boiling, giving carbonate and dinitrotoluol; from this it would seem probable that our bromine acid was more stable than that containing no bromine, as our ammonium salt (the sodium or potassium salt could not be obtained) stood unaltered for many days, and even could be warmed on the water-bath for some minutes with only slight decomposition. The curious change of color with sodic hydrate observed by us did not occur with the dinitro body, confirming our conclusion that this action was due to the removal of bromine by the sodic hydrate.

Argentie Metabromdinitrophenylacetate,



This substance was prepared by adding a solution of argentic nitrate to a solution of the acid in ammoniac hydrate, which had been freed from the excess of ammonia as completely as possible, best by using an excess of the acid in preparing the salt. The heavy flocculent precipitate, which, if the solutions were strong, entirely filled the liquid, and even piled up above its surface, became crystalline on standing, and was purified by washing with cold water. Some of the salt is also formed when argentic nitrate is added to an aqueous solution of the free metabromdinitrophenylacetic acid. The analysis of the salt gave the following results.

0.3530 gram of the air-dried salt lost, when heated to 100° , 0.0149 gram.

	Calculated for $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2)_2\text{CH}_2\text{CO}_2\text{Ag}\cdot\text{H}_2\text{O}.$	Found.
Water,	4.19	4.22

I. 0.1674 gram of the salt dried at 100° gave, after being heated with fuming nitric acid in a sealed tube¹ and precipitated with potassic bromide, 0.0761 gram of argentic bromide.

II. 0.1556 gram of the salt treated in the same way gave 0.0707 gram of argentic bromide.

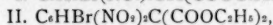
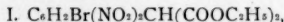
	Calculated for $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2)_2\text{CH}_2\text{CO}_2\text{Ag}.$	I.	Found.	II.
Silver,	26.21	26.11		26.10

¹ We had hoped in this way to determine both the silver and bromine in one operation, but found that the filtrate gave a precipitate with potassic bromide. It would seem, therefore, that the presence of an excess of argentic nitrate is necessary to retain all the bromine.

Properties.—The argentic bromdinitrophenylacetate forms white flat prisms terminated by a single plane at an oblique angle; the terminated end is somewhat broader than the other, so that the crystals look like a flattened base-ball bat. They have also a tendency to twin longitudinally. When put in the flame of a Bunsen lamp they burn with a sparkling flame, but when heated carefully on a piece of porcelain decompose quietly, leaving a residue of silver. The substance is very slightly soluble in cold water, so that it can be washed without too great loss; more soluble in hot water, from which it crystallises apparently without decomposition; insoluble in cold alcohol, but slowly decomposed if heated with it.

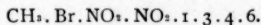
Constitution of Bromdinitrophenylmalonic Ester.

The formation of metabromdinitrotoluol from bromdinitrophenylmalonic ester by a series of reactions giving essentially a quantitative yield and taking place at temperatures not above 150° , throws a great deal of light on the nature of this substance. In the first place, its conversion into a toluol derivative is a welcome confirmation of the formula which we have given it, and which did not rest on the most secure experimental foundations. In our first paper it was stated that the analysis left the choice open between the following formulas,

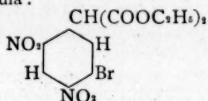


and we decided in favor of the first on account of the analyses of the sodium salt, an amorphous substance for the purity of which we had no guarantee, and also on account of the ease with which this salt was formed and decomposed, the product of the decomposition being the original ester. Against this formula stood only our inability at the time to explain the reactions by which it was formed, an objection which is removed by this paper. The easy conversion of a substance having Formula I into a toluol compound is to be expected, whereas with one having Formula II it would be necessary to add two atoms of hydrogen, an action which could hardly take place quantitatively by boiling with dilute sulphuric acid, or distillation with steam, the two processes employed in converting the bromdinitrophenylmalonic ester into the bromdinitrotoluol. This formation of the substituted toluol therefore establishes Formula I beyond question.

In the second place, the way is opened to the determination of the position of the substituting radicals upon the benzol ring in all these compounds, as their position must be the same as in the bromdinitrotoluol. Messrs. W. B. Bentley and W. H. Warren have accordingly, at our request, determined the constitution of the bromdinitrotoluol by replacing its bromine successively by the amido group and by hydrogen, and have found in this way that its constitution is



For the details of their work we would refer to their paper which will follow the present one. It follows from this that in the tribromdinitrobenzol $\text{Br} \cdot \text{H} \cdot \text{Br} \cdot \text{NO}_2 \cdot \text{Br} \cdot \text{NO}_2 \cdot 1 \cdot 2 \cdot 3 \cdot 4 \cdot 5 \cdot 6$, the bromine numbered 1, which stands in the ortho position to one nitro group and the hydrogen, in the para position to the other nitro group, has been replaced by the malonic ester radical $\text{CH}(\text{COOC}_2\text{H}_5)_2$; that the bromine replaced by hydrogen is the one between the two nitro groups; and that the third bromine, which is in exactly the same relation to the nitro groups as the one replaced by the malonic ester radical, is left entirely unaltered. This last fact seems very strange to us. The constitution of our bromdinitrophenylmalonic ester is therefore represented by the following graphical formula:



Contributions from the Chemical Laboratory of the Department of Agriculture.

XIV.—ANALYSES OF THE SEED OF CALYCANTHUS GLAUCUS.

By H. W. WILEY.

Botanical Data.

Natural Order Calycanthaceae. Shrubs, with opposite, simple, entire, exstipulate leaves. Flowers purple, sometimes pale, sweet-scented, solitary, terminating short branches. Sepals and petals

similar, indefinite, united below into an inversely conical cup. Stamens indefinite, inserted on the inner margin of the cup. Pistils distinct, indefinite, one or two ovuled, inserted on the sides and bottom of the cup within. Fruit made up of one to many achenia enclosed in the enlarged calyx-cup. Species four, all American.

C. floridus, L. Leaves oval to oblong, softly downy beneath. Rich uplands from North Carolina to Mississippi.

C. glaucus, Willdenow. Leaves oblong-ovate to ovate-lanceolate, conspicuously taper-pointed, glaucous beneath, roughish above. North Carolina to Georgia, in the mountains.

C. laevigatus, Willdenow. Leaves oblong, either blunt or taper pointed, bright green and glabrous or nearly so on both sides. Flowers 1 to 1½ inches long. Pennsylvania and southward along the Alleghanies.

C. occidentalis, Hooker & Arnott. Leaves of the form of *C. laevigatus*, not shining beneath, glabrous above. Flowers one inch or more long. Northern California and northward.

The seeds are in pods, from eight to sixteen in each pod.

The weight of one hundred seeds unhulled was found to be 21.1964 grams. The average weight of each seed is therefore about 200 milligrams.

In preparing the seeds for analysis they were first removed from the pod and then carefully hulled. The pods, hulls and kernels were examined separately.

The pods and hulls were ground in a drug mill and passed through a ½ mm. mesh sieve. On account of the great quantity of oil in the kernels it was found impracticable to treat them as described above. They were therefore reduced to as fine a powder as possible on an iron plate ore pulveriser and the oil removed by petroleum spirit. After the removal of the spirit the deoleated residue was ground to a fine flour and passed through a ½ mm. mesh sieve.

The analyses of the pod, hull and kernel gave the following data:

Composition of the Pod.

	Per cent.
Moisture, ...	9.03
Petroleum spirit extract, ...	3.07
Sulphuric ether extract, ...	3.25
Absolute alcohol extract, ...	1.73

	Per cent.
80 per cent. alcohol extract, ...	1.87
Fibre insoluble in dilute acid and alkali, ...	29.26
Albuminoids, ...	5.25
Ash, ...	4.24
Digestible fibre, starch and undetermined, by difference, ...	42.26

Composition of the Hulls.

	Per cent.
Moisture, ...	11.39
Petroleum spirit extract, ...	1.22
Sulphuric ether extract, ...	0.30
Absolute alcohol extract, ...	0.54
80 per cent. alcohol extract, ...	1.09
Albuminoids, ...	2.63
Fibre insoluble in dilute acid and alkali, ...	30.71
Ash, ...	1.72
Digestible fibre, starch, etc. (by difference), ...	50.40

Composition of the Unextracted Kernels.

	Per cent.
Moisture, ...	5.36
Petroleum spirit extract, ...	47.08
Ether extract, ...	1.29
Absolute alcohol extract, ...	9.69
80 per cent. alcohol extract, ...	2.48
Fibre, ...	1.36
Ash, ...	1.08
Albuminoids, ...	23.62
Digestible fibre, starch, and by difference, ...	8.05

Composition of the Extracted Kernels.

	Per cent.
Moisture, ...	3.52
Petroleum spirit extract, ...	3.64
Ether extract, ...	0.31
Absolute alcohol extract, ...	17.33
80 per cent. alcohol extract, ...	6.33
Fibre, ...	2.85
Ash, ...	4.69
Albuminoids, ...	42.31
Digestible fibre, starch, and by difference, ...	13.00

The above data show that the kernel of the calycanthus possesses remarkable qualities. The small quantity of undetermined substances is not remarkable when it is remembered that a considerable quantity of albuminous matter is extracted by alcohol, and is therefore counted twice in the summary. The same remark may be applied to the alkaloid present in the seed which will be described further on. The almost entire absence of starch is a noteworthy characteristic of the calycanthus flour. When a small portion of it is boiled with water, cooled and treated with a solution of iodine, only a faint reaction is produced. Starch is therefore present in extremely small quantities.

The percentage of oil is very large. Dr. Eccles, to whose discovery of the alkaloid I will soon refer, reported 39 per cent. of oil. We found in most careful extractions with petroleum spirit, over 47 per cent. Add to this the portion given up to ether and it is seen that practically the hulled seed is one-half ether extract. The character of this oil is described further on.

The large proportion of albuminoids is also a marked property of the seed. It contains nearly twice as much of this valuable substance as wheat.

The quantity of sugar (dextrose, sucrose and dextrine) in the seed is also large, and from the analysis it is easy to see why the "bubby" berries are so greedily sought after by cattle.

The separation and determination of the different sugars has not yet been completed.

Oil from Calycanthus Seed.

The oil from calycanthus seed has a beautiful faint yellow color, and when extracted with an appropriate solvent and purified, a peculiar odor.

The specific gravity of the purified oil, extracted by petroleum spirit, compared with water at the boiling point, was found to be .9058. The specific gravity of the expressed oil in similar conditions was .9110. The higher specific gravity of the expressed oil was doubtless due to a trace of moisture which it contained, it having been simply warmed and filtered before the specific gravity was taken.

Five grams of the oil tested for volatile acid showed the absorption of only .2 cc. of N/10 barium hydrate solution. The oil may therefore be said to be entirely free from volatile acids.

The iodine absorption of the oil was found to be as follows :

For the crude expressed oil, 129.53 per cent. ; for the purified extracted oil, 128.66 per cent. In respect of its iodine coefficient, therefore, calycanthus oil occupies a mean position between cotton and flaxseed oils.

The crystallising point of its fatty acid was found to be 12.5°.

Judging by its iodine coefficient, calycanthus oil would be a mild drying oil, but no experiment to determine this point has yet been made. The iodine absorption being so much greater than would be required for olein alone, shows the presence of lin-oleic acid or some homologue thereof.

The refractive index of the oil determined by the Pullfrick refractometer at 28° is 1.47351. The index of pure water determined at the same degree is 1.33338.

The Alkaloid in Calycanthus Seed.

Dr. R. G. Eccles, of Brooklyn, N. Y., has discovered in the seed of the calycanthus an alkaloid which he has named calycanthine. His attention was called to this substance by a paper of E. E. Sterns on "The Fruit of Calycanthus," published in the "Bulletin of the Torrey Botanical Club," for August, 1888, p. 205. The poisonous character of these seeds was called to the attention of Mr. Sterns by Mr. J. H. H. Boyd, of Cagle, Tenn., in a letter written November, 1887. Mr. Boyd's letter is as follows :

"Hundreds of cattle and sheep have died here in the past five years from 'bubby' (the eccentric name of the shrub). The seeds only are poisonous. When a brute gets a sufficient dose, from five to ten well-filled pods, it makes for the nearest water and often falls dead while drinking, or it may live three or four weeks and then die. The symptoms are like those of a man extremely drunk, except that any noise frightens it. Stamp the ground hard close to a brute poisoned with 'bubby,' and it will jump and jerk and tremble for several minutes. That is our method of telling when they have taken it. The eyes turn white and glassy, and while lying they throw back the head and look as if dead already. 'Bubby' does not seem to hurt a brute so much if it cannot get water. Our best remedy is apple brandy, strong coffee and raw eggs poured down as soon as possible after finding. It is certain that 'bubby' is the most poisonous of any shrub or weed in existence here, from the fact that when brutes have once

eaten it they will take it every time they can get it. It grows on every hillside, along all branches (creeks), in every fence corner and almost everywhere."

Dr. Eccles' first paper was published in the "Western Druggist" of January, 1889, on p. 15. The alkaloid in the seeds is evidently not a very virulent one, since twenty of the seeds were eaten without any toxic symptoms being manifested. The alkaloid is described in this paper as being slightly soluble in water and very soluble in ether or chloroform. Its salts are insoluble in the latter substance, but very soluble in water. Its most characteristic color is the development of a green color on the addition of strong nitric acid. A second paper by Dr. Eccles was published in the "Druggist's Circular and Chemical Gazette" for March, 1888, on p. 65. He describes the method of extracting the alkaloid as that of Dr. Lyons.

"The finely powdered seeds were first macerated for twenty-four hours, with occasional shaking in a mixture of ether, alcohol and ammonia. After allowing the mixture to settle, the clear solution was decanted and evaporated to a small bulk, then stirred or shaken with dilute sulphuric acid and concentrated ether. This was again evaporated until all the ether was gone, when it was filtered. The clear acid solution was neutralised with ammonia shaken up with ether, allowed to settle, the ether decanted from the surface into a porcelain evaporating basin, where it was allowed to spontaneously evaporate and leave the alkaloid. This alkaloid, for several hours after the last of the ether had gone, had a strong, distinct odor of pyridine, so that it was probably contaminated with that volatile alkaloid of tobacco."

The alkaloid in some of the seed having first been extracted by alcohol until it gave no further test, it was treated with a little sulphuric acid, by which an additional alkaloid was extracted, leading Dr. Eccles to suppose the existence of more than one in the plant. Dr. Eccles also states that the acid solution of the alkaloid precipitated by ammonia did not yield the alkaloid by shaking with ether, an experience which is entirely contrary to my own. About 2 per cent. of the alkaloid was found by Dr. Eccles.

Mr. Boyd wrote to the Department in March, 1889, for information in regard to the calycanthus poison, and at his instigation I communicated with Dr. Eccles on the subject. He kindly gave me all the information which he had in regard to the matter, and under date of March 20, 1889, wrote as follows:

"I hated to give the investigation up, as it has just reached the most interesting point, but you know the saying, 'man proposes and God disposes.' After the rush is over, say some three months hence, I will do some work on the subject, and would therefore beg you to let me know from time to time what you discover."

Since that time I have not seen any report of any further work of Dr. Eccles, and my contribution at the present time is certainly not intended to take the place of any investigation which he has made or may make in the matter. The methods which I used in isolating the alkaloid are as follows:

Alkaloid in Extracted Oil. Since nearly all the alkaloids are more or less soluble in fixed oil, I was led to suppose that the calycanthus seed, containing so large a percentage of fixed oil, might yield some of its alkaloid to that oil on extraction with petroleum spirit. To see if this assumption were true, a portion of the extracted oil, after being freed as nearly as possible from petroleum, was shaken with an equal volume of dilute sulphuric acid (1 to 50) and the acid liquid separated from the oily layer. This acid solution was shaken with petroleum ether to remove any fat which it might contain. The residual acid solution was made strongly alkaline with ammonia and shaken with ether. The ethereal solution was evaporated and the alkaloid thus obtained dissolved in dilute sulphuric acid, and treated with a solution of iodine in potassium iodide. A dense brown precipitate indicated the presence of an alkaloid.

500 grams of the oil were next washed with 1000 cc. of dilute sulphuric acid (1 to 50) in successive portions. The acid washings were shaken with petroleum to remove any trace of oil. The solution was then made strongly alkaline with ammonia and shaken four times with 150 cc. of ether. The ether was evaporated in a tared dish, and the extract dried at 100° was found to weigh .1366 gram. The percentage of alkaloid, therefore, in the oil was .027.

The above reaction shows that the amount of alkaloid extracted by the oil, when the latter is removed by petroleum ether from the seed, while important from a chemical point of view, would not appreciably affect the quantitative determination of the alkaloid in the seed.

Alkaloid in the Seed. The seeds were carefully removed from the hulls and the two substances examined separately for alkaloids and bitter principles.

Alkaloid in the Kernel. The seeds removed from the hulls were powdered as finely as possible, considering their oily state. The fat was then extracted by means of petroleum spirit. The dry residue was finely powdered and passed through the fine mesh sieve employed in the preparation of vegetable substances for analysis. 10 grams of the powdered seed were then weighed into each of six flasks. The first flask was treated with 100 cc. of ether; the second with 100 cc. of alcohol, 95 per cent.; the third flask with 100 cc. of chloroform; the fourth with a mixture of ether, alcohol and ammonia; the fifth with 100 cc. of dilute sulphuric acid (1 to 50); the sixth flask with equal parts of ether and alcohol. The flasks were all tightly corked and placed in a warm room, the temperature of which was 35°. They were shaken at frequent intervals for four days, and then treated as follows:

The liquid portions of Nos. 1, 2, 3, 4 and 6 were filtered into evaporating dishes, and the filter papers containing a portion of the solid substance were returned to the flasks. The same quantity of the reagents was again added and the flasks treated in the same way as indicated. The residue was then washed with frequent shaking by the same quantity of the particular reagent used for each one. The finely powdered seed was thus extracted for six days with the solvents, and washed thoroughly with the same solvent.

No. 5, containing the sulphuric acid reagent, was found to be in the state of an emulsion. It was therefore found impossible to filter off the liquid portion. The whole mass was made strongly alkaline with ammonia, and treated at once with 200 cc. of ether. The emulsion separated very slowly, but after its separation the ether layer was poured off into an evaporating dish and evaporated to dryness. This treatment with ether was repeated eight times, and the whole of the ethereal solution evaporated in the same dish. Abundant crystals of the alkaloid were shown by the first evaporation. The alkaloidal extracts from all the samples were then treated as follows:

They were thoroughly washed in successive portions of dilute sulphuric acid (1 to 50), about 100 cc. of the acid being used in all. The acid washings were then shaken in a separatory tube twice with 50 cc. of ether, and the ethereal layer removed. In this way the solution was freed entirely of fat and other substances soluble in ether, including, perhaps, a trace of the sulphate of the

alkaloid. The remaining portion was now made strongly alkaline with sodic hydrate, and shaken with successive portions of ether of about 50 cc. each for five times. The extracts, which were now in a very pure state, with exception of No. 1, were evaporated to dryness in tared glass dishes and weighed. The percentages of alkaloid obtained by the six different methods were as follows:

No. 1,		0.79	per cent. alkaloid, very impure.
" 2,		1.20	" " " pure.
" 3,		1.85	" " " "
" 4,		2.35	" " " "
" 5,		4.25	" " " "
" 6,		0.22	" " " "

In No. 4, only one extraction-of four days was made. In treating the residue the second time with 100 cc. more of the same reagent the flask was broken. The high percentage obtained shows that this method of extraction completed would have yielded almost as large a percentage of the alkaloid as was obtained in No. 5.

The residue from Nos. 1, 2, 3 and 6, of the above samples, were treated with dilute H_2SO_4 for twenty-four hours, filtered out, and re-extracted with same reagent. The acid solutions were treated as in No. 5, and the percentages of alkaloid obtained were as follows:

No. 1,		1.98	per cent. alkaloid, pure.
" 2,		0.76	" " " "
" 3,		1.30	" " " "
" 6,		1.83	" " " "

The alkaloid thus extracted by H_2SO_4 did not show any difference in composition from the other extracts.

Another extraction was made by forming a paste of the flour with lime, and extracting with an equal mixture of ether and alcohol under pressure at 80° . The percentage of alkaloid obtained by this treatment was 2.58 (alkaloid pure). The residue was neutralised and treated as in the other cases by dilute H_2SO_4 . The percentage of alkaloid obtained was 0.39 per cent.

The percentages of total alkaloid obtained in all extractions were:

No. 1,		2.77	per cent.
" 2,		1.96	"
" 3,		2.15	"
" 4,		2.35	"
" 5,		4.25	"
" 6,		2.05	"
" 7,		3.07	"

General Properties of the Alkaloid.

Calycanthine crystallises from ether in feathery masses on the sides of the dish, presenting the appearance of a diminutive pine forest. These feathery crystals form very rapidly and present a beautiful appearance. On slower evaporation the bottom of the dish is found to be covered with triangular crystals which appear to be hemihedrae from oblique octohedrae. The exact crystalline structure will be shortly determined.

Specific Rotatory Power.

The alkaloid being practically insoluble in alcohol and water, the determination of its specific rotatory power is deferred until the properties of its salts can be studied.

Percentage Composition.

The following numbers were obtained for the percentages of the elementary substances present in the alkaloid:

Carbon,		42.13 per cent.
Hydrogen,		7.75 "
Nitrogen,		16.22 "
Oxygen (by difference),		33.77 "

The above figures lead to the following formula for calycanthine, $C_{18}H_{40}O_{11}N_6$.

	Calculated for $C_{18}H_{40}O_{11}N_6$.	Found.
C	41.86 per cent.	42.13 per cent.
H	7.75 "	7.89 "
N	16.28 "	16.22 "
O	34.11 "	33.76 "

Alkaloid in the Hulls. Ten grams of the hulls were examined for alkaloids by extraction with dilute H_2SO_4 and subsequent treatment as indicated above.

The percentage obtained was .83. The alkaloidal principle was amorphous, but contained traces of calycanthine as revealed by the color tests to be mentioned. The nature of the amorphous alkaloidal principle has not yet been determined.

Color Reactions. Calycanthine exhibits the most remarkable series of color tests of any known alkaloid.

Dr. Eccles described the beautiful green color produced by

nitric acid. In extending these tests I obtained the following results:

H_2SO_4 , pale yellow.

HNO_3 , bright green (persistent).

$\text{H}_2\text{SO}_4 + \text{C}_{12}\text{H}_{22}\text{O}_{11}$, (sucrose) fine purple (persistent and changing finally to blue).

$\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$, fine blood-brick red.

Dextrose, maltose, etc., gave also the furfural reaction, but without so marked a purple as with sucrose.

The presence of sugar in the seed renders it possible to secure the furfural reaction in the raw seed by the simple application of H_2SO_4 .

The examinations necessary to complete the investigations, and to determine the crystalline forms of the alkaloids and the properties of its compounds with common acids, will be made at as early a date as possible. We hope also to be able to study its physiological effects.

In these investigations I have been assisted by Messrs. Horton, Trescott, Krug and Sanborn.

ON A VOLUMETRIC METHOD OF GENERAL APPLICABILITY FOR THE DETERMINATION OF COMBINED SULPHURIC ACID.

BY LAUNCELOT W. ANDREWS.

Of the volumetric methods at present in use for the determination of sulphuric acid, none can be considered entirely satisfactory, although some of them are very useful for technical purposes. Several of these methods involve a double titration, some require three standard solutions,¹ and others are only applicable in the absence of bases precipitable by sodium carbonate.

The author believes, therefore, that the presentation of a new method, applicable in the presence of magnesium, calcium, alumi-

¹ Precht, *Ztschr. anal. Chem.*, 1879, 521.

num, zinc, manganese, iron (ferric), nickel, cobalt, and silver, which requires but one standard solution with a single titration, and which in precision is at least equal to the ordinary gravimetric determination as barium sulphate, while demanding much less time for its execution, will not be thought superfluous.

The process depends upon the following series of reactions: First, to the solution of a sulphate is added an excess of a solution of barium chromate in hydrochloric acid; second, the solution is neutralised with ammonia or calcium carbonate, and filtered; third, the filtrate is acidified with hydrochloric acid, potassium iodide added, and the free iodine titrated with decinormal sodium thiosulphate solution (1 cc. = 12.654 mg. iodine = 2.662 mg. SO_2).

The barium chromate employed may contain barium sulphate, but must be completely freed from soluble chromates and from barium carbonate, nitrate or chloride, by prolonged washing, first with boiling water slightly acidified with acetic acid, finally with hot distilled water, until the washings give no precipitate with sulphuric acid, and (in a quantity of 100 cc.) a barely perceptible reaction with hydrochloric acid, potassium iodide and starch paste.¹

A suitable solution of the barium chromate is prepared by digesting it with hydrochloric acid containing 36 grams acid in the litre. This solution will contain from 2 to 4 per cent. of barium chromate, according to the temperature at which it was prepared.

The reagent being ready, the analysis is performed as follows:

The sulphate to be determined is diluted, if necessary, until it does not contain more than 2 per cent., at most, of sulphuric anhydride, is made approximately neutral, and is heated to boiling. While boiling hot, an excess of the barium chromate solution is gradually introduced, and the boiling continued one minute, or longer, if carbonates were present.

The precipitate of barium sulphate is always yellow from the barium chromate which it carries down with it, provided sufficient excess of the latter reagent was added.

Calcium carbonate, which must be entirely free from barium or

¹When barium chloride is precipitated with an excess of potassium chromate, the water with which the precipitate is washed will, for a long time, show a yellow color. This is not, as has been supposed, due to the solubility of BaCrO_4 , but to the fact that it obstinately retains soluble chromate. According to the author's observations, barium chromate is not sufficiently soluble in water to impart any color to the latter. According to the mean of four concordant determinations, one million parts of water dissolve 15 parts barium chromate at 18°.4 C.

strontium carbonates or calcium sulphate, is then thrown in small portions into the still hot liquid until no further evolution of carbonic anhydride is observed, and the boiling continued one or two minutes. The solution is filtered while hot, and the precipitate is washed with a small quantity of hot water until the washings are colorless, and a little longer. Under these conditions the barium chromate has no tendency to run through the filter or to retain any soluble chromate. 75 cc. of water will usually be found more than sufficient to effect the washing.

If, on the other hand, the solution is allowed to stand over night with the precipitate in it, calcium chromate will be retained and a longer washing becomes necessary. In this case the results may come somewhat too high, in consequence of the necessarily large amount of wash-water dissolving an appreciable quantity of barium chromate. Under normal conditions the error from this source is quite insignificant.

The filtrate, after cooling, is treated with a sufficient amount of crystals of potassium iodide (free from iodate) and with 5 to 7 cc. fuming hydrochloric acid for each 100 cc. of liquid. This amount of acid is enough to induce a prompt and complete reduction of the chromate, but not enough to decompose the starch paste. It is advisable to run in the decinormal sodium thiosulphate from a burette until the brown color of the iodine is nearly discharged before adding the starch, and then to continue the titration slowly, with constant stirring, until the turning point is reached.

The above process must be modified in the presence of ferric, nickel, or zinc salts by using ammonia instead of calcium carbonate to neutralise the acid liquid. The solution in this case is to be made distinctly alkaline, and the excess of ammonia boiled nearly away before filtering. The necessity for this modification arises from the fact that if a ferric or nickel or zinc salt is boiled with a chromate and calcium carbonate, basic chromates of iron and nickel are precipitated, from which the chromic acid cannot be removed, or only with difficulty, by washing. Barium chromate, when precipitated from its acid solution by ammonia, does not possess the agreeable properties which it shows when thrown down by calcium carbonate. It is much more finely divided than in the latter case, tends to run through the filter, which must therefore be double or of very dense paper, and requires a longer washing to remove the soluble chromates which it more tena-

ciously retains; consequently, ammonia is only to be used when the employment of calcium carbonate is inadmissible. It is not practicable to precipitate the excess of barium chromate with sodium acetate from hydrochloric acid solution. Numerous experiments, the details of which it is not worth while to give, show that barium chromate is so soluble in hot dilute acetic acid¹ that the results fall 3 to 5 per cent. too high, while if precipitated cold and allowed to stand, the results are too low.²

The following analyses show the applicability of the method:

I. Taken 10 cc. of a solution containing 20.8984 grams pure and dry ammonium sulphate per litre. Diluted to 50 cc., treated with 15 cc. BaCrO_4 solution and with CaCO_3 , as described above.

Required 47.60 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol. = .1267 gram SO_2 found. Calculated, .1266 gram SO_2 ; 100.08 per cent. found.

II. Taken 10 cc. of the same ammonium sulphate solution and treated as in No. I. Required 47.60 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol.

The volume of the solution before titration was 300 cc. 100.08 per cent. found.

III. 20 cc. of the same ammonium sulphate solution, treated as before, required 95.50 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol.

Total volume of the solution, 400 cc.; 100.37 per cent. found.

IV. Taken .2980 gram $\text{CuSO}_4 + 5\text{H}_2\text{O}$, small crystals obtained by triple recrystallisation of a commercial sample. The copper was precipitated from boiling sol. with $(\text{NH}_4)_2\text{S}$ (free from sulphate), solution boiled with acetic acid to expel H_2S , filtered and filtrate treated as above.

35.95 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol. required = .0957 gram SO_2 = 32.11 per cent. found. Theoretical per cent. = 32.09.

V. Taken 10 cc. $(\text{NH}_4)_2\text{SO}_4$ solution (see I) containing .20898 gram, diluted to 100 cc., treated with 20 cc. BaCrO_4 sol. as above and neutralised with ammonia. Required 47.30 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol. = .1260 gram SO_2 instead of .1266 gram. Found 99.52 per cent.

VI. Taken .6485 gram $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 + 24\text{H}_2\text{O}$. Treated as No. V. Required 80.65 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol. = .2147 gram SO_2 . Calculated .2153 gram SO_2 . Found 33.11 per cent. SO_2 . Theory 33.20 per cent.

VII. *a*. Taken 100 cc. of the Iowa City water supply. Treated as No. V. Required 2.10 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol.

¹ Compare Morse, this Journal 2, 176.

² The method cannot be used in the presence of phosphoric acid, and, of course, all reducing agents, as well as bismuth and copper salts, must be excluded.

b. Taken 200 cc. ditto, ditto. Required 4.30 cc. $\frac{1}{10}$ $\text{Na}_2\text{S}_2\text{O}_3$ sol. Found 56 mg. and 57 mg. SO_3 per litre. A gravimetric analysis gave 58 mg. SO_3 per litre.

It seems probable that an indirect determination of sodium and potassium would be possible by weighing these elements as sulphates and determining the sulphuric anhydride volumetrically as described. Experiments to test this are now in progress. If feasible, it is evident that it would often be more convenient than the usual indirect determination as chlorides, while free from some of the well known sources of error involved in the gravimetric determination of sulphuric acid in the presence of alkalies.

It is both a duty and a pleasure for me to take this opportunity to express publicly my thanks to Mr. F. W. Spanutius, instructor in chemistry here, for the zeal and skill with which he has assisted me in the experimental part of this investigation. Some of the test analyses given above were performed by him.

THE UNIVERSITY OF IOWA, November 16, 1889.

REVIEWS AND REPORTS.

ON THE NATURE OF TELLURIUM.¹

The atomic weight of tellurium, as determined thus far, appears to be greater than that of iodine, though the results obtained by different investigators vary between wide limits. Berzelius found 128.9 and 128.3, v. Hauer 127.9, and Wills 126.39–129.66. ($\text{O}=16$ is used as the standard throughout the paper.) But from the arrangement of the elements according to the periodic system we should expect tellurium to fall in the same family as sulphur and selenium, and therefore to have an atomic weight of about 123.5, lying between that of antimony (119.96) and that of iodine (126.86). The author undertook the present investigation in order to make a thorough revision of the atomic weight of tellurium. The tellurium used was prepared from various Hungarian ores and from Hungarian crude tellurium, being carefully purified in each case, and finally distilled in a current of hydrogen. The

¹ Abstract of a paper by B. Brauner: Chem. Soc. Journ. 1889, 382.

element as thus obtained possessed the properties required of pure tellurium according to the present state of our knowledge.

Many different methods were tried for the determination of the atomic weight. Several of these were, however, abandoned on account of the great experimental difficulties encountered. Three of the methods involved the synthesis of a telluride (of copper, silver, or gold), but it was found impossible to obtain these compounds in pure condition on account of the tendency of the metals to take up an excess of tellurium which could scarcely be driven off at a yellow heat.

The results which the author considers reliable were obtained by the methods described below.

1. *Oxidation of tellurium with aqua regia.*—Weighed quantities of tellurium were treated with nitrohydrochloric acid and the solution was evaporated to dryness, care being taken to prevent the escape of any tellurium tetrachloride which might be volatilised. The residue was then evaporated several times with nitric acid and finally heated to 440° . The resulting dioxide was weighed. Five experiments gave $\text{Te} = 125.0\text{--}126.4$. It was observed that when the tellurium dioxide was treated, after weighing, with hydrochloric acid, a *white insoluble residue* was always left.

2. *Conversion of tellurium dioxide into the basic sulphate.*—The dioxide was treated with hydrochloric acid, and the solution (always containing some undissolved white substance) was evaporated to dryness with a slight excess of sulphuric acid. Crystals of the basic sulphate $\text{Te}_2\text{O}_5 \cdot \text{SO}_3$ were thus obtained. Three experiments gave $\text{Te} = 125.0\text{--}127.5$.

3. *Conversion of tellurium into the basic sulphate.*—The tellurium was weighed as such, converted into the dioxide, and the dioxide then converted into the basic sulphate. Six experiments gave $\text{Te} = 124.6\text{--}127.1$.

4. *Analysis of tellurium tetrabromide.*—The tetrabromide was prepared by adding powdered tellurium to pure bromine, and then removing the excess of bromine by warming the mixture and passing through it a current of dry carbon dioxide. The product was found to contain some tellurium which had been protected from the action of the bromine. On heating together tellurium and tellurium tetrabromide, the dibromide is formed, thus: $\text{TeBr}_4 + \text{Te} = 2\text{TeBr}_2$. It was found possible to separate the dibromide from the tetrabromide by fractional sublimation in a vacuum, the dibromide being entirely volatilised and driven out of the tube at 200° . On afterwards raising the temperature to about 300° the tetrabromide sublimed. A weighed quantity of this tetrabromide was dissolved in a solution of tartaric acid, and the bromine then precipitated as silver bromide with certain special precautions. One experiment gave (after the method had been perfected) $\text{Te} = 127.61$.

The results obtained by the methods above described varied so greatly that the author was led to attempt to decompose tellurium by several methods of fractionation.

First method.—Tellurium tetrabromide was sublimed as before, but in two portions. The percentage of bromine was then estimated by a combined gravimetric and volumetric method, which was found to give excellent results. The amount of silver necessary for each precipitation was calculated, accurately weighed, and dissolved in nitric acid. After adding the silver nitrate to the tartaric acid solution of the tetrabromide, the resulting precipitate was agitated for many hours in the dark to rid it from the impurities which it held. After clearing the liquid, the *very small* excess of silver or bromine present was estimated by standard decinormal solutions. The more volatile portion gave $\text{Te} = 127.60$ and 127.63 , while the less volatile portion gave $\text{Te} = 127.59$ and 127.63 . These results, as will be seen, agree perfectly with that obtained before by the simple gravimetric method.

Second method.—Crude tellurium after being dissolved was precipitated by sulphurous acid. It was then fused with potassium cyanide, dissolved, and precipitated fractionally by a current of air. Each portion was then distilled separately in a current of hydrogen, converted into the tetrabromide and analysed as before.

Fraction No. I gave $\text{Te} = 127.67$ and 127.67 .

Fraction No. II gave $\text{Te} = 127.60$.

Fraction No. IV gave $\text{Te} = 127.64$ and 127.67 .

Third method.—A hydrochloric acid solution of pure tellurium dioxide was precipitated fractionally with ammonia (fractions I–VIII) and then with sulphurous acid (fraction IX). Each fraction was then converted into the tetrabromide and analysed.

Fraction No. I gave $\text{Te} = 127.60$.

Fraction No. IV gave $\text{Te} = 127.71$.

Fraction No. IX gave $\text{Te} = 127.57$.

The different fractions as obtained by these three methods seem identical.

Tellurium tetrabromide was then prepared from tellurium which had been carefully purified and finally fused in a current of hydrogen, but not distilled. The tetrabromide was separated from the dibromide by subliming the latter in a vacuum, but was not itself sublimed, being found to decompose. Its color was greenish, while the tetrabromide made from tellurium which has been *distilled* in a current of hydrogen has an orange color. Three analyses gave $\text{Te} = 129.63$, 137.72 , and 128.88 .

The results show that "if tellurium, obtained by any process of fractionation whatever, be subjected to distillation in a current of hydrogen, and the tetrabromide be prepared from this by sublimation in a vacuum, its analysis always gives the same atomic weight for tellurium. If, however, the tellurium be only fused in a current of an indifferent gas, and the tetrabromide be not sublimed, higher numbers will be obtained."

5. *Analysis of tellurium dibromide.*—The dibromide was prepared by fusion of the tetrabromide with an excess of tellurium and subsequent sublimation in a vacuum. Its appearance under different conditions seems to show that it is a mixture either of several allotropic modifications or of different substances. The bromine was estimated gravimetrically. Four experiments gave $\text{Te} = 130-133$.

From the widely divergent results obtained by these different methods for the determination of the atomic weight the author concludes that *tellurium is not a simple substance*.

The difference in composition and properties between the tetrabromide prepared from tellurium distilled in a current of hydrogen and that prepared from tellurium which has not been distilled, makes it appear very probable that one constituent of tellurium escapes, partly, during the distillation.

Having found it necessary to prepare pure silver for use in these researches, the author undertook to determine the amount of oxygen occluded by the metal when obtained by one of the methods of Stas. The silver after precipitation with ammonium sulphite and digestion with ammonia, was fused with borax and nitre, and poured into a mould of kaolin, the bars thus formed being afterward carefully freed from any external impurity.

Silver prepared in this way was heated nearly to its melting point and allowed to cool. It was then placed in a combustion tube, heated to 150° , and pure dry air drawn over it for some time. One end of the tube was then sealed and the air exhausted by a Sprengel pump. After standing over night it was again exhausted, and when a vacuum as perfect as possible was obtained, the tube containing the silver was heated to 450° , the pump acting all the time, and the gas given off being collected. A red heat was then applied, and the tube was pumped out at this temperature for six hours. 153.2133 grams of silver were used.

Up to 450° there was given off .219 cc. of gas (reduced to normal conditions). Above 450° there was given off .844 cc. of gas. This was analysed by means of microeudiometers, and found to consist of .586 cc. of oxygen and .298 cc. of nitrogen. Now, .298 cc. of nitrogen corresponds to .312 cc. of air, so that the amount of oxygen given up above 450° was .532 cc.

A similar experiment using no silver gave .249 cc. of gas collected. Another experiment was made, using the silver of the previous experiment. In this case the silver was allowed to cool in a vacuum, then heated to 150° , and air drawn over it. This, when heated again to redness in a vacuum, gave .215 cc. of gas (air) collected. Now, .249 and .215 are practically identical with .219, the amount obtained up to 450° in the first experiment, and this is therefore to be neglected.

The experiments show that 153.2133 grams of silver heated to redness in a Sprengel vacuum give off .312 cc. of air (probably

condensed) and .532 cc. of oxygen, so that the composition of the metal used was

Silver, ...	99.9995
Oxygen, ...	.0005
	100.0000

As the very slight impurities of the undistilled silver of Stas, .003-.006 per cent., were not regarded by him, it is evident that his researches "do not require the correction proposed by Dumas, due to an occlusion of oxygen in silver, its quantity being practically nought."

C. E. SAUNDERS.

THE CONDITION OF MATTER IN THE VICINITY OF THE CRITICAL POINT.

A communication by Cailletet and Colardeau in reference to this subject has recently been published.¹ They have made some interesting investigations, and the conclusions deduced therefrom may prove of considerable importance, especially in the problem of the liquefaction of gases.

In 1822 Cagniard de La Tour observed that when liquids are heated in sealed tubes, the surface of demarcation between liquid and gas disappears at a certain temperature, which differs with the liquid used.² He inferred that, at that temperature, the liquid is completely converted into vapor in the space in which it is confined. In accordance with this view, the critical temperature would be that at which a sudden discontinuity is occasioned—the temperature above which the liquid state ceases to exist. But Ramsay, in 1880, expressed the opinion that the liquid state continues above the critical temperature; and it is to this matter that the attention of Cailletet and Colardeau is first directed. The following experiment, described by them, tends to confirm Ramsay's opinion. A small quantity of iodine is deposited, by vaporisation, in the upper part of a tube used for compression of carbon dioxide. As soon as the carbon dioxide that has been liquefied attains such a level as to come in contact with the iodine, it assumes a color similar to the color of a solution of iodine in chloroform, while the gaseous carbon dioxide above, though in contact with the solid iodine on the walls of the tube, remains perfectly colorless. Now, on heating the tube above 31° (the critical temperature of carbon dioxide), the meniscus disappears; the color, however, is not diffused through the entire length of the tube, but remains just where it was before—that is, in that portion of the tube occupied by the liquid carbon dioxide before the tube was heated. In the vicinity of the place from which the meniscus has disappeared the color is gradually less distinct, but the upper

¹Ann. chim. phys. (6) 17, 269.

²Ibid. (2) 21, 127.

part of the tube remains perfectly colorless. This seems to indicate that only the surface of the liquid has disappeared, and that the liquid continues to exist, as such, in the lower part of the tube. Spectroscopic examination indicates that, after the critical temperature is reached, the iodine is still dissolved in a liquid, and not in a gas.

The following facts lead to the same conclusion as the above. Let a tube partly filled with liquid carbon dioxide be heated to and above the critical temperature of the same. The pressure increases with the temperature, and, with the data thus obtained, a curve can be traced which will represent the gradual change in tension of the vapor as the temperature rises. Now, it is found that such a curve above the critical temperature is simply a prolongation of the curve below the critical temperature. But, if at the critical temperature total vaporisation had taken place, then, starting at this temperature, the vapor would no longer have been saturated, and the curve representing its expansion would not be a prolongation of the curve of saturated vapor. Furthermore, if several similar experiments be made, using in each case the same tube but different quantities of liquid carbon dioxide, the curves traced will cease to be identical as soon as the critical temperature is attained. This, also, shows that the liquid state must continue beyond the critical temperature. It is evident that if the liquid had been completely vaporised at this temperature, the curves would in each case continue to be identical. On the other hand, if the liquid state continued, vaporisation continued beyond the critical temperature; the vapor was still saturated, and hence the greater the quantity of liquid remaining in the tube at the critical temperature, the more rapidly would the tension increase after this temperature was attained. In consequence of this, the curves would cease to be identical just at the critical temperature.

A few years ago Jamin offered the following hypothesis as an explanation of the conduct of a liquid when heated in a sealed tube. As the temperature rises, the density of the liquid diminishes by reason of its expansion; meanwhile, the quantity of superposed vapor rapidly increases, and its density increases. At a certain temperature the density of liquid and vapor must become equal. Just at this temperature the surface of demarcation becomes indistinct, and the liquid, having lost all its weight, floats in an atmosphere of the same density, forming with it a genuine emulsion. Now, on continuing to heat the tube after the disappearance of the meniscus, the density of the liquid must continue to decrease and that of the vapor to increase. The density of the vapor will become greater than that of the liquid, and a phenomenon just the reverse of the above should be observed, that is to say, the liquid should collect in the upper part of the tube and the gas in the lower part. This second part of Jamin's hypothesis has been the occasion of numerous experiments, but

the results have always been negative, although the temperature has been raised to such an extent as to cause fracture of the tubes.

An experiment by Cailletet and Colardeau occasioned serious doubt in regard to Jamin's hypothesis. This was followed by another experiment which seems quite conclusive as to this matter, and may be described as follows: In the two branches of an O-tube which contains a quantity of sulphuric acid more than sufficient to fill the lower curvature, carbon dioxide is compressed. The height of the sulphuric acid in the two branches of the tube is the same. On cooling one branch of the tube, the greater part of the carbon dioxide condenses to a liquid in that branch, while a portion condenses in the other branch. Under these conditions there is a considerable depression of the level of the sulphuric acid in that branch which contains the larger quantity of liquid carbon dioxide. When the tube is gradually heated in a bath of tepid water the difference in height of the sulphuric acid in the two branches diminishes somewhat, but even at the critical temperature this difference does not by any means entirely disappear, as would have been the case if, at that temperature, the density of the liquid had become equal to that of the superposed vapor. This experiment also proves that the critical temperature is not, as Cagniard de La Tour supposed, that temperature at which total vaporisation takes place; for, if this were true, the height of the sulphuric acid at the critical temperature would, of course, have been the same in both branches of the tube. When the tube was cooled it was observed that more carbon dioxide condensed to a liquid in that branch in which more of the liquid was previously contained, an additional proof of the continuation of the liquid state above the critical temperature.

Cailletet and Colardeau draw the following conclusions from their investigations: 1. The critical temperature of a liquid is not that temperature at which the liquid suddenly and completely vaporises in the space in which it is confined. The liquid state continues above that temperature. 2. It is not that temperature at which the liquid and its saturated vapor have the same density. 3. It is that temperature at which the liquid and the gaseous atmosphere above it become susceptible of mutual solution in all proportions, forming, after agitation, a homogeneous mixture. This conclusion applies to the critical point as observed by increase of pressure on mixtures partially liquefiable (such, for example, as mixtures of carbon dioxide and air), as well as to that observed by the elevation of the temperature of a liquid.

Since the liquid state continues above the critical temperature, it follows that, in order to liquefy a gas, it is not absolutely necessary to reduce the temperature lower than its critical temperature. When the pressure is sufficient, liquefaction must take place above this temperature, the liquid dissolving in the still non-liquefied gaseous mass. In the case of carbon dioxide this has been veri-

fied by Cailletet and Colardeau. Under a pressure of 80 to 100 atmospheres, and at a temperature about 9° above its critical temperature, liquefaction took place, as was indicated by solution of some iodine that had been deposited in the tube in which the experiment was performed.

When a liquid contained in a sealed tube is heated to its critical temperature, the meniscus, just prior to its disappearance, seems to grow thicker and to diffuse itself. Soon, however, the contents of the tube become apparently homogeneous. Now, on cooling, a little cloud is observed in the same part of the tube, which vanishes as the meniscus reappears. These phenomena Cailletet and Colardeau attribute to the reciprocal solution of gas and liquid in the neighborhood of the surface of demarcation. Just at this moment the tube contains all possible transitions from a perfect liquid at the base to a perfect gas at the summit.

C. C. BLACKSHEAR.

THE REACTIONS OF HYDROGEN PEROXIDE WITH CHROMIC ACID AND THE CHROMATES.

In the September (1889) number of the *Annales de Chimie et de Physique*, M. Berthelot reports his investigations upon the above subject. A brief abstract of his paper is here given.

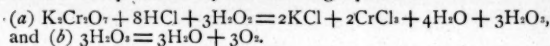
Barreswil was the first to call attention to the blue coloration produced by the action of hydrogen peroxide upon potassium bichromate and gave the name of "perchromic acid" to the blue substance soluble in ether. He believed its composition to be represented by a symbol which would now be written HCrO_4 . Moisson concluded that the substance is a compound of chromic acid and hydrogen peroxide; M. Berthelot, that it is a compound of perchromic acid and hydrogen peroxide.

When potassium permanganate and hydrogen peroxide are brought together, each loses the same amount of oxygen; it makes no difference whether the peroxide be added to the permanganate, or *vice versa*. In the case of hydrogen peroxide and potassium bichromate, on the other hand, the character of the reaction depends upon which of the two substances is in excess. If the peroxide is added to the mixture of bichromate and hydrochloric or sulphuric acid, and the solutions are extremely dilute, scarcely a trace of perchromic acid is formed, and the peroxide and bichromate, in being simultaneously reduced, lose equal quantities of oxygen. If, on the contrary, the bichromate is added to the peroxide—the latter being thus in excess—the blue coloration is noticed, and the amount of peroxide decomposed by a given quantity of bichromate is greater than when the operation is conducted in the former way—the ratio between the amounts of oxygen lost by the peroxide and bichromate being 1.52-1.63:1. These results were the same whether hydrochloric or sulphuric acid is used, and whether the acid is mixed with the bichromate

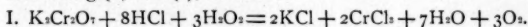
or with the peroxide. The quantity of acid taken was just that amount necessary to convert the products of the reduction of the bichromate into potassium and chromium chloride or sulphate. If nitric acid is used the evolution of oxygen is more rapid; but the result is practically the same.

If in adding the peroxide to the excess of bichromate, or the bichromate to the excess of peroxide, care is not taken to have the solutions very dilute and to add very slowly, there will be an excess of the *added solution* at certain points, and here the reaction will take place in a different way from the main reaction. The variation in the relative quantities of oxygen given off (as given above) is probably due to this condition.

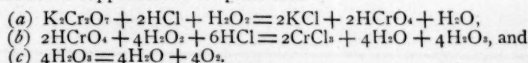
Following M. Berthelot's reasoning, it appears probable that, when the peroxide is added to the bichromate in excess, the reaction is represented by the following equations:



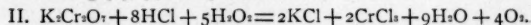
Combining (a) and (b), we have



When the bichromate is added to the peroxide in excess the reaction is supposed to take place thus:



Combining (a), (b) and (c), we have



On comparing equations I and II it will be noticed that the ratio between the quantities of peroxide decomposed by a given quantity of bichromate = 3:5 or 1:1.66, which is near the figure obtained by M. Berthelot in actual experiment. The variation is probably due, as stated above, to the fact that at some points the reaction took place according to equation I, while the principal decomposition was that represented by equation II. A calorimetric determination showed that when the peroxide is added to the bichromate the heat evolved is 45.2 cal.; when the bichromate is added to the peroxide, 66.8 cal.

When a very weak acid, such as boric or hydrocyanic acid, is used instead of one of the strong mineral acids, a brown coloration is produced, which at once changes to blue on adding sulphuric acid. Such acids as phosphoric and acetic give the blue color, sometimes mixed with the brown, yielding, however, the blue color alone on addition of sulphuric acid. This brown color M. Berthelot believes to be due to the formation of a compound of chromium chromate and hydrogen peroxide. If an extremely dilute solution of pure chromic acid is treated with hydrogen peroxide the brown color alone is noticed.

When hydrogen peroxide is brought together with pure potassium bichromate the color changes to an intense brown, then effervescence begins, and finally the solution slowly assumes again its original color. A fresh addition of peroxide produces the same effects as the first—the bichromate is left undecomposed, the solution containing at the end of the experiment no trace of perchromic acid or of chromic salt. Pure potassium chromate decomposes hydrogen peroxide, though more slowly than the bichromate, the salt being found unchanged at the end of the experiment. In order to ascertain whether the decomposition of the peroxide is due to the formation of an intermediate product, M. Berthelot brought together solutions of the peroxide and bichromate and, while the reaction was in progress, added dilute ammonia. A precipitate consisting of chromic oxide, ammonium chromate and hydrogen peroxide was thrown down. The supernatant solution was decanted off and the precipitate repeatedly washed with pure water. The precipitate decomposed rapidly, however, coloring the wash-liquor yellow and giving off bubbles of oxygen. The presence of each of the three constituents was nevertheless proved. The action would, therefore, seem to consist in the formation of an unstable compound through the simultaneous reduction of the peroxide and the bichromate, and in the reformation of the bichromate with the reduction of still more peroxide. If pure chromic oxide, in the presence of potash, is treated in the cold with hydrogen peroxide, a precipitate similar to that described is formed and this decomposes with the formation of potassium chromate. In the presence of ammonia the same kind of transformation takes place, the action, however, being extremely slow in cold solution.

W. W. RANDALL.